Synthesis of New Energetic Materials

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FOREWORD

This final report, entitled "Synthesis of New Energetic Materials," presents the results of a study performed by the University of North Texas, Department of Chemistry, Denton, TX 76203-0068, under Contract No. F29601-92-K-0018, for Operating Location AC, Phillips Laboratory (RKS), Edwards AFB, CA 93524-7048. The Project Managers for Phillips Laboratory were Dr. E. J. Wucherer and Dr. Patrick G. Carrick.

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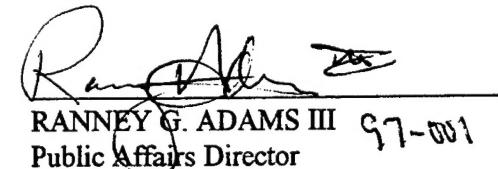
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Work on the synthesis of new hydrocarbon fuel systems involved: (a) a study of the synthesis and acid-promoted rearrangement of PCU-derived pinacols; (b) synthesis of an HCTD-derived pinacol; (c) a study of the generation and trapping of a PCU-derived vinylidenecarbene; (d) synthesis of "homosecohexaprismane-10,13-dione"; (e) synthesis and thermal rearrangement of pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]trideca-2,6-diene; (f) a study of the acid and base promoted rearrangements of hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione. The results of studies that were performed in collaboration with investigators in four external laboratories are described. In addition, two new syntheses of TNAZ were developed, both of which proceed by way of an intermediate 1-azabicyclo[1.1.0]butane. Finally, X-ray crystal structures have been determined for a variety of cage hydrocarbons.

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GLOSSARY

^{1}H NMR	proton nuclear magnetic resonance spectrometry
HCl	hydrochloric acid
HCTD	heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane
HTPB	hydroxy-terminated polybutadiene
KOH	potassium hydroxide
MO	molecular orbital
MOLPAK	MOLecular PAcKing computer program
Ms$_2$0	methanesulfonic anhydride
PCU	pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane
PM3	PM3 Hamiltonian, used in semiempirical molecular orbital calculations
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
Tf$_2$0	trifluoromethanesulfonic anhydride
THF	tetrahydrofuran
TNAZ	1,3,3-trinitroazetidine
TPE	thermoplastic elastomer
α-HMX	α-polymorph of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
β-HMX	β-polymorph of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane

1.0 ABSTRACT

During the tenure of this project, progress on hydrocarbon fuel synthesis has accrued in three distinct areas: (i) large-scale synthesis of new high energy/high density hydrocarbon fuel systems; (ii) development of improved routes for the large-scale synthesis of 1,3,3-trinitroazetidine (TNAZ); (iii) structural studies of energetic hydrocarbons and their synthetic precursors. Work on the synthesis of new hydrocarbon fuel systems involved: (a) a study of the synthesis and acid promoted rearrangement of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCU)-derived pinacols; (b) synthesis of an heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (HCTD)-derived pinacol; (c) a study of the generation and trapping of a PCU-derived vinylidenecarbene; (d) synthesis of "homosecohexaprismane-10,13-dione"; (e) synthesis and thermal rearrangement of pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]trideca-2,6-diene; (f) a study of the acid and base promoted rearrangements of hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione. The results of studies that were performed in collaboration with investigators in four external laboratories are described. In addition, two new syntheses of TNAZ were developed, both of which proceed by way of an intermediate 1-azabicyclo[1.1.0]butane. Finally, X-ray crystal structures have been determined for a variety of cage hydrocarbons.

2.0 INTRODUCTION

2.1 Large-Scale Synthesis of New High Energy/High Density Hydrocarbon Fuel Systems

Work at the University of North Texas has been directed toward the synthesis of new polycarbocyclic hydrocarbon systems that are of interest as a potential new class of high energy/high density fuel systems for volume-limited military applications. Compounds of this type generally possess unusually high, positive standard heats of formation and unusually high densities.[1] The objective was to synthesize compounds of this general type in 50 to 500-gm quantities.

An example in this regard is provided by the titanium-promoted reductive dimerization[2,3] of pentacyclic monoketones and their monomethylated analogs, as indicated in Scheme 1. These compounds were successfully prepared in relatively large quantities (i.e., several hundred gm). Samples were sent to a number of laboratories for evaluation of their fuel properties and combustion characteristics.

Scheme 1

1a (R = H)
1b (R = Me)
(mixture of isomers)

TiCl₄, Zn
pyridine, THF
reflux 22 h

2a (R = H)
2b (R = Me)
("PCU alkene dimer", mixture of isomers)
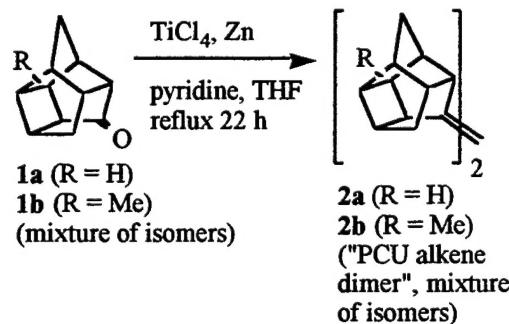
Although alkene dimers possess the potential to develop into useful fuel systems, it is first necessary to prepare them in relatively large quantities and to thoroughly evaluate their fuel properties and combustion characteristics. Whereas compounds of this type are relatively available in multigram quantities, it will be necessary to develop new methodology for scaling up existing reactions to afford kilogram quantities of the desired materials.

In collaboration with Professor Herman Ammon (University of Maryland), computational methods were utilized to predict the crystal densities of (i) several isomerically pure monomethylated pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCU) alkene dimers and (ii) several polycyclic epoxides. The crystal densities calculated from X-ray crystal structure data were compared

with the corresponding calculated values. By using advanced theoretical methods, attempts were made to address any discrpancies that may exist between computed densities and those derived from X-ray data.

2.2 Improved Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine (TNAZ)

In collaboration with Dr. Thomas G. Archibald (Aerojet Corporation, Propulsion Division, Sacramento, CA), several routes for the synthesis of 1,3,3-trinitroazetidine (TNAZ) were investigated. Of these, the most promising new method employed additions of various reagents, X-Y, across the highly strained C(3)-N σ-bond in 3-ethyl-1-azabicyclo[1.1.0]butane. In the course of this study, it was found that reaction of this highly strained bicyclic amine with *in situ* generated HNO_2 resulted in addition across the C(3)-N σ-bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording *N*-nitroso-3-ethyl-3-nitroazacyclo-butane (54%), which was oxidized subsequently to the corresponding dinitroazetidine, *N*-nitro-3-ethyl-3-nitroazacyclobutane (89%). These observations provided the basis of the method by which a novel synthesis of TNAZ was developed, as described herein.

In 1969, Funke reported the synthesis of 3-ethyl-1-azabicyclo[1.1.0]butane and some aspects of its chemistry.[4,5] Since that time, relatively little interest has been shown in this unusual ring system. Our own interest in this compound stems from its potential use as a key intermediate in the synthesis of *N*,3-disubstituted azetidines, which otherwise can be quite difficult to obtain [e.g., via S_N2 displacements on *N*-substituted-3-tosyloxy- (or -3-mesyloxy-) azdetidines].[6] Compounds of this type have attracted attention in recent years among members of the energetic materials community.[7,8] In addition, natural products chemists have been attracted to azetidine alkaloids, a class of strikingly bioactive compounds that have been isolated from marine organisms.[9] Finally, some unusual transformations of 3-functionalized azetidines that are of mech-anistic interest have been reported recently.[10,11]

As a first step toward understanding the chemistry of the 1-azabicyclo[1.1.0] ring system,[12,13] reactions of 3-ethyl-1-azabicyclo[1.1.0]butane with a variety of electrophiles were investigated; e.g., N_2O_4, $ClCO_2Et$, Tf_2O, and Ms_2O. In each case, the observed reaction product(s) resulted from addition of the reagent, X-Y, across the highly strained C(3)-N σ-bond in the substrate, thereby affording new *N*-,3-disubstituted azetidines. The range of reagents studied has now been extended in an effort to explore the scope and limitations of reactions of this type. In the course of this work, several of the addition reactions were performed in aqueous solution in an effort to design environmentally benign (i.e., "green") synthetic routes to novel 3-substituted azetidines.

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2.3 Structural Studies of Energetic Hydrocarbons and Their Synthetic Precursors

The level of understanding of the structural factors that contribute to the crystal densities and total energy content of compact, strained polycarbocyclic cage systems has been aided materially through acquisition and subsequent analysis of X-ray crystal structures, which have been obtained for several of the new energetic materials and their synthetic precursors. This work was made possible by productive collaborations with three structural laboratories: (i) Prof. Simon G. Bott, Department of Chemistry, University of North Texas; (ii) Prof. William H. Watson, Department of Chemistry, Texas Christian University; (iii) Prof. Herman L. Ammon, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD.

3.0 METHODOLOGY, RESULTS, AND DISCUSSION

3.1 Large-Scale Synthesis of New High Energy/High Density Hydrocarbon Fuel Systems

3.1.1 Synthesis and Acid Promoted Rearrangement of PCU-Derived Pinacols. The results obtained from the study of the acid promoted pinacol rearrangements of **3a**, **4a** and **4b** are illustrated in Scheme 2.[14] These results indicate that in all three pinacol rearrangements, the cyclobutane ring [via C(7)-C(8) σ-bond migration] appears to display higher migratory aptitude than does an *endo* norbornyl group [whose migration would involve 1,2-shift of the C(8)-C(9) σ-bond in the protonated pinacol substrate].[14]

Scheme 2

4a: X = CH$_2$
4b: X = spirocyclo-
         propyl

6a: X = CH$_2$
6b: X = spiro-
         cyclopropyl

4
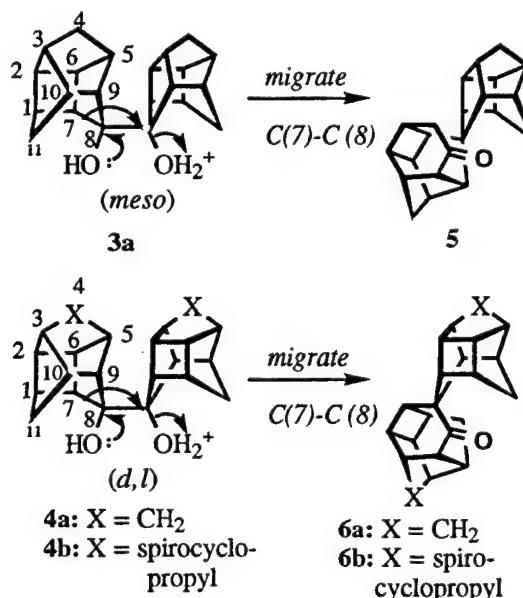
A molecular mechanics conformational search[*] of protonated diol **3a** found three low-energy conformations. Analysis of the torsion angles $C(7)-C(8)-C(8')-OH_2^+$ and $C(9)-C(8)-C(8')-OH_2^+$ of the lowest energy conformation, which is populated to the extent of 90% at 25 °C (as gleaned from the Boltzmann distribution), indicated that the $C(7)-C(8)$ σ-bond lies in a more nearly antiperiplanar relationship to the protonated OH group than does the $C(8)-C(9)$ σ-bond. On this basis the $C(7)-C(8)$ bond is expected to display the higher migratory aptitude, as was observed experimentally.[14]

3.1.2 Synthesis of an HCTD-Derived Pinacol. Sodium-promoted reductive dimerization of 12-methyleneheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecan-7-one (**7**) in dry tetra-hydrofuran (THF) afforded the corresponding "pinacol", i.e., **8** (Scheme 3). The structure of **8** was established unequivocally via single-crystal X-ray structural analysis.[15]

Scheme 3
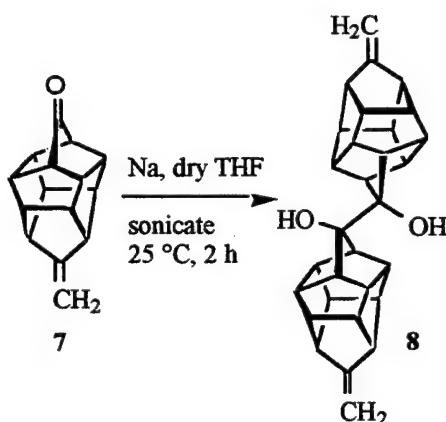
3.1.3 Generation and Trapping of a PCU-Derived Vinylidenecarbene. Recently, PCU-8-vinylidenecarbene (**10a**) was generated via reaction of 8-bromomethylene-PCU (**9**) with *n*-BuLi. Interestingly, when this reaction is performed in the presence of an alkene trapping agent (i.e., cyclohexene), a cage-functionalized *exo*-methylenecyclopropane, **11**, is obtained as the only product. Compound **11** was characterized via its conversion to the corresponding dichlorospiro-(cyclopentane), **12** (Scheme 4), whose structure was established unequivocally via single crystal X-ray structural analysis.[16]

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[*]Molecular mechanics calculations were performed by using GMMX, version 1.0, which is available from Serena Software, Box 3076, Bloomington, IN 47402. The MMX force field was used for this calculation, and a mixed statistical search on both bonds and coordinates was performed.

No experimental evidence was found for the formation of products that might have resulted via alkene trapping of a putative cycloalkyne intermediate in this reaction. Interestingly, the results of semi-empirical molecular orbital (MO) calculations (PM3) indicated that **10b** is only *ca.* 0.4 kcal/mol less stable than **10a**, but that the energy barrier for rearrangement of **10a** to **10b** is relatively high (>30 kcal-mol^{-1}).[16]

3.1.4 Synthesis of Hexacyclo[7.4.0.0^{2,8}.0^{3,7}.0^{4,12}.0^{6,11}]tridecane-10,13-dione ("Homo-secohexaprismane-10,13-dione", 20). Compound **20** was prepared via a six-step reaction sequence that resulted in homologation of two of the cyclopentane rings in PCU-8,11-dione (**13**). The complete synthesis, shown in Scheme 5, has been published.[17]

Scheme 4

6
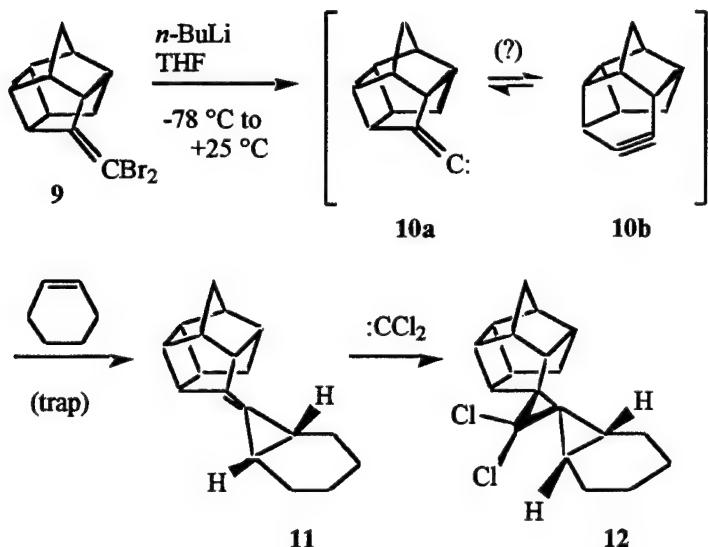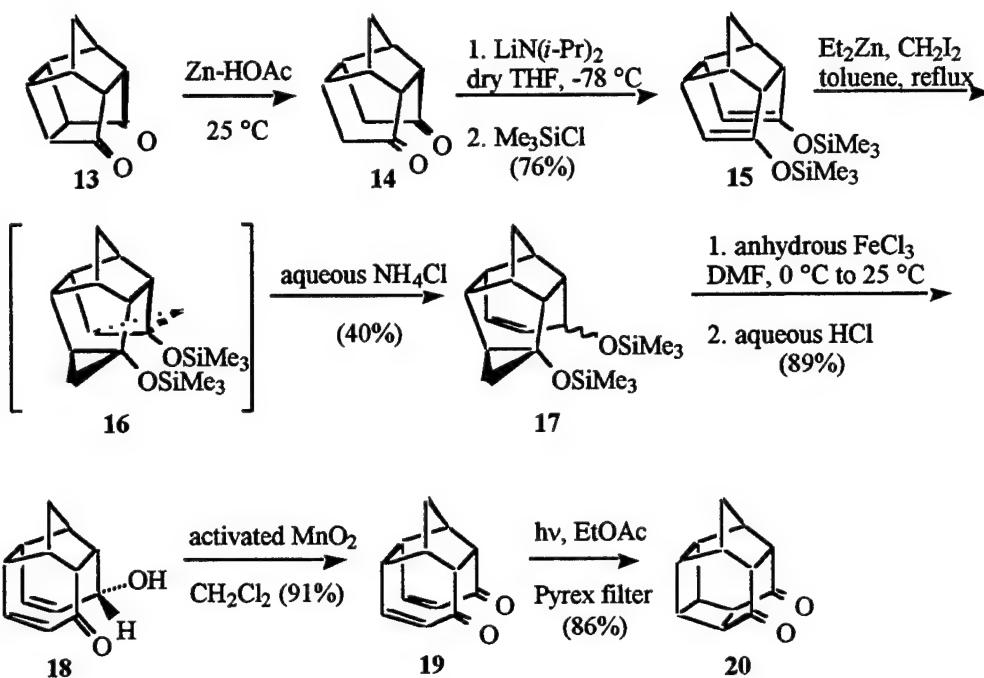
Scheme 5

3.1.5 Synthesis and Thermal Rearrangement of Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-trideca-2,6-diene (27). Compound **27** was synthesized in five steps from 1-hydroxyhexacyclo[6.5.0.0^{2,6}.0^{3,11}.0^{5,10}.0^{9,12}]tridecan-7-one (**21**). The complete synthesis, shown in Scheme 6, has been published.[18]

Compound **27** undergoes thermal rearrangement to pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]-trideca-7,12-diene (i.e., "[2.2.1]triblattadiene", **29**, Scheme 7). The intermediacy of *cis,cisoid,cis*-tricyclo[7.4.0.0^{2,7}]trideca-3,5,10,12-tetraene (**29**) in the thermal rearrangement of **27** was inferred via analysis of the ¹H NMR spectrum of partially rearranged **27** and subsequently was further established via the results of a trapping experiment (i.e., fluorene was produced when thermal rearrangement of **27** was performed in the presence of 10% Pd/C).[18]

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Scheme 6

21

NaBH₄, EtOH
0 °C, 1 h (85%)

22a: X = OH, Y = H
22b: X = H, Y = OH

TsCl, py
CH₂Cl₂
(80-100%)

23a: X = OTs, Y = H
23b: X = H, Y = OTs

NaH, THF
25 °C
(71-98%)

24

NaBH₄, EtOH
25 °C, 12 h
(93%)

25

Ms₂O, CH₂Cl₂
reflux 19h (30%)

26

(-MsOH)

27

hν

28 *(not formed)*

Scheme 7

27

120-150 °C
DMSO-d_6

28

H₂, Pd/C, Δ
(trap reaction intermediate)

(fluorene)

28

intramolecular Diels-Alder reaction

29 ("[2.2.1]triblattadiene")

8
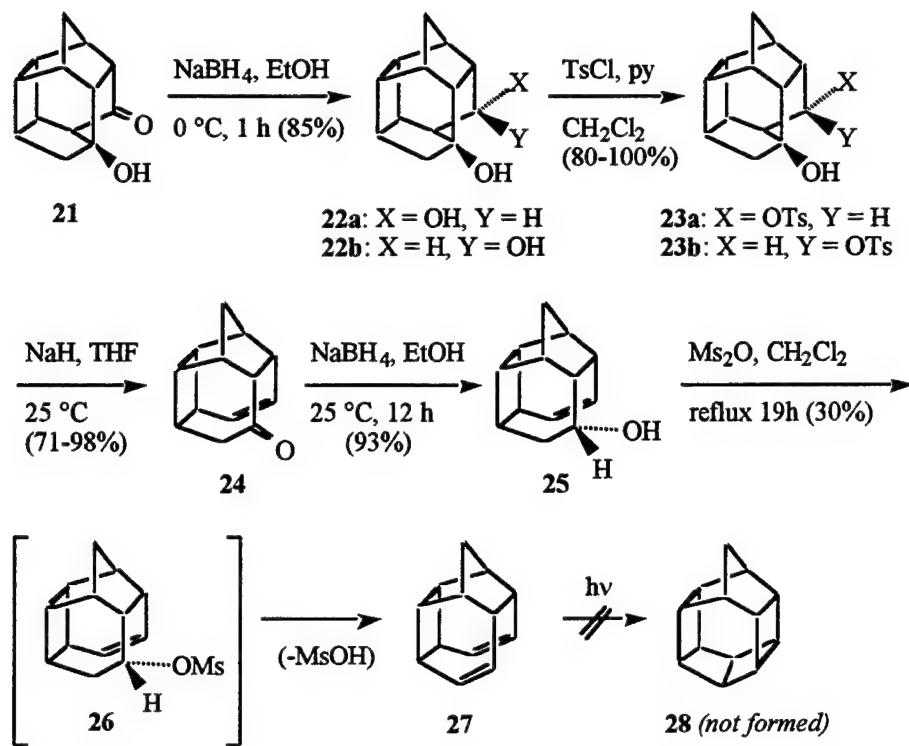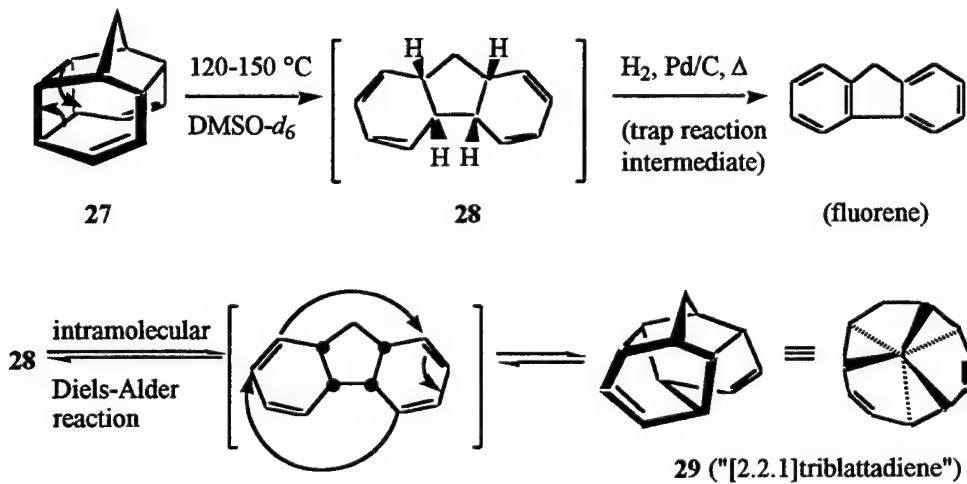
3.1.6 Acid and Base Promoted Rearrangements of Hexacyclo[11.2.1.0²,¹².0⁵,¹⁰- .0⁵,¹⁵.0¹⁰,¹⁴]hexadeca-6,8-diene-4,11-dione (32). Compound **32** was prepared via BF₃ promoted ring homologation of hexacyclic cage diketone **30**[19] with ethyl diazoacetate (Scheme 8). Subsequent reaction of a toluene solution of **32** with a catalytic amount of HCl resulted in extensive skeletal rearrangement, thereby affording 6,7-benzotetracyclo-[7.3.0.0⁴,¹².0⁵,¹⁰]dodecane-2,6-dione (**33**, Scheme 8).[20] In addition, **32** reacted smoothly with ethanolic KOH at ambient temperature (in 3 h) or at reflux (in 0.5 h) to afford a rearranged product, **34** (Scheme 8).[20] The structures of **33** and **34** were established unequivocally via application of single crystal X-ray crystallographic methods.[20]

Scheme 8
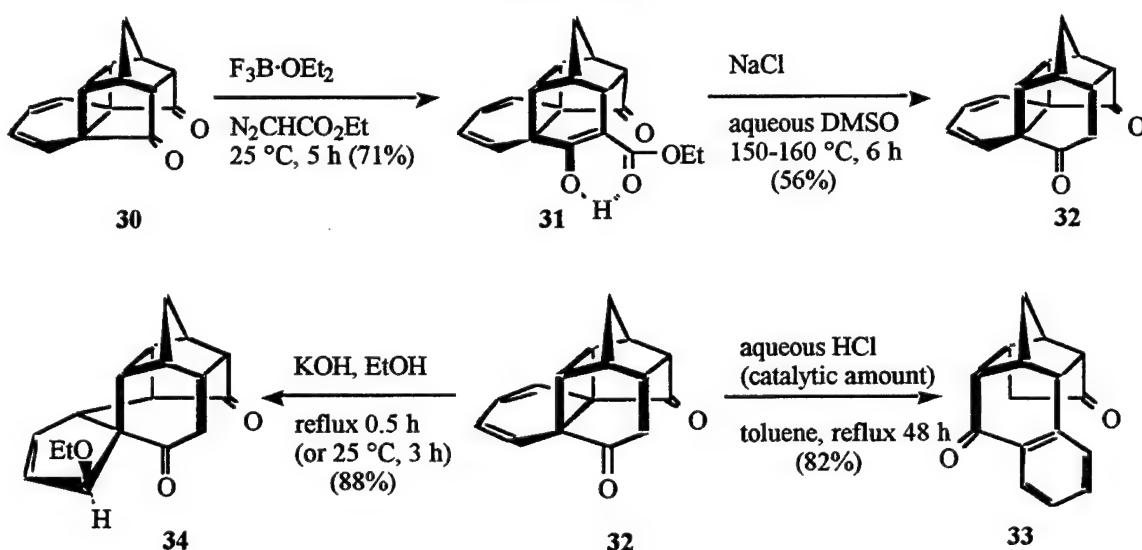
3.1.7 Collaborations with Other Laboratories. In an effort to begin evaluating the fuel properties of new high energy density materials, active collaborations with a number of laboratories were initiated during the tenure of this contract. A description of each of these collaborative efforts follows.

Dr. Rodney L. Willer (Thiokol Corporation). A collaborative project was undertaken with Dr. Rodney L. Willer and his associates at Thiokol Corporation (Elkton Division) to investigate the potential use of mixtures of isomeric methylated PCU alkene dimers as crystalline modifiers for thermoplastic elastomer (TPE)-based solid propellant binders. Together with Dr. Willer, an improved binder was developed for solid explosives and propellants, a major ingredient of which is a mixture of methylated PCU alkene dimers. The resulting castable solid propellant formula-tion displayed desirable processing and mechanical

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properties; e.g., it can be processed at elevated temperatures, and it solidifies via physical rather than chemical (i.e., cross-linking) mechanisms. A patent resulted from this study.[21]

Dr. Herman L. Ammon (Department of Chemistry, University of Maryland, College Park, MD). The importance of high density as a feature of potential fuel systems that seek to maximize net volumetric heat of combustion is well-documented. The prediction of the crystal density of an unknown compound typically has been approached through the use of "volume additivity" procedures.[22-25] Here, the crystal-molecular volume (V_{cm}) is calculated by summing appropriate crystal-atomic or group volumes (V_{ca}):

$$V_{cm} = \Sigma V_c \tag{1}$$

and the corresponding crystal density is obtained by dividing the molecular mass (M) by V_{cm}; thus,

$$r = M/V_{cm} \tag{2}$$

V_{ca} values are usually obtained by least-squares procedures that fit V_{cm} values to experimental crystal-molecular volumes (V_{ce}) from X-ray crystal structure data (V_{ce} = unit cell volume divided by the number of molecules per unit cell).

Volume additivity methods generally do not take into account crystal packing efficiency or molecular conformation effects and, thus, will afford identical calculated densities for positional and conformational isomers and for compounds that possess different multiples of the same functional group composition. As an example, a volume additivity calculation predicts that 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (α-HMX and β-HMX) will all possess the same crystal density, 1.783 g-cm^{-3}.[25] In fact, the experimentally observed densities of these three compounds differ markedly (i.e., 1.806,[26] 1.839,[27] and 1.902,[28] respectively).

Recently, Holden, Du, and Ammon[29] reported a procedure for predicting possible crystal structures of C, H, N, O, and F-containing organic compounds. Their approach involves construction of crude crystal packing arrangements (MOLPAK = MOLecular PAcKing program), starting with an optimized model (search probe) for the compound of interest, by positioning molecules around a central molecule into predetermined coordination sphere geometries. The best of these arrangements are refined, subsequently, with a crystal lattice energy minimization (WMIN)[30] program. This procedure takes molecular shape, conformation, and crystal packing efficiency into account.

As part of this study, crystal density modeling calculations were performed for four isomeric methylated PCU alkene dimers by using the MOLPAK-WMIN approach.[29] The observed and calculated crystal densities generally agree within 1 to 2%.[31] More recently, these crystal density modeling calculations have been extended to include several epoxide-functionalized tetrahydro- and hexahydromethanonaphthalenes.[32]

Dr. G. J. Kabo (Belorussian State University, Minsk, Belarus). Highly purified samples of heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (HCTD, **36**), and PCU (**37**, Scheme 9) were sent to Dr. Kabo for study of their thermodynamic properties. The results of this study have been published in two papers which appeared in *J. Chem. Thermodynamics* (1994[33] and 1995[34]).

Scheme 9

36   37
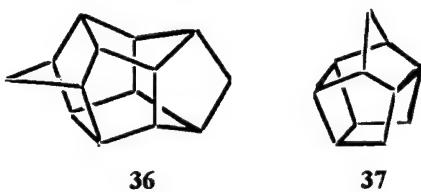
Dr. Corin Segal (Department of Aerospace Engineering, Mechanics and Engineering Science, University of Florida). Dr. Segal and members of his research group at the University of Florida have evaluated the combustion characteristics of mixtures of isomeric PCU alkene dimers (**2a**) as solid fuels in compressible flows. Subsequently, Dr. Segal extended these studies to include evaluation of **2a** as a solid fuel under conditions of high shear flow. Samples of the mixture of isomeric PCU alkene dimers were cured with a styrene-polybutadiene copolymer (10% w/w) binder on the test chamber wall and ignited convectively via a gaseous flame in air at Mach 0.12-0.25 at a stagnation temperature and pressure of 300 K and 150-250 kPa, respectively. Ignition times and rates of heat release were measured. The results indicated that, when compared with hydroxy-terminated polybutadiene (HTPB) fuel under the same thermodynamic conditions and geometrical configuration, **2a** ignition times are an order of magnitude more rapid. The heat released during combustion of **2a** is more than twice as great as that of HTPB fuel under comparable conditions. A manuscript that presents the results of this study has been accepted for publication (in press, 1996).[35] Varying quantitites of four different candidate energetic hydrocarbon fuel systems (i.e., **2a**, **2b**, **11**, **34**, and **35**; see Scheme 10) have been sent to Dr. Segal for his combustion studies.

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Scheme 10

Compound	Quantity	Compound	Quantity
2a (R = H) 2b (R = Me) (mixtures of isomers)	**2a**: 261 grams **2b**: 240 grams	**34** (mixture of isomers)	2 grams
35 (mixture of isomers)	20 grams	**11**	12 grams
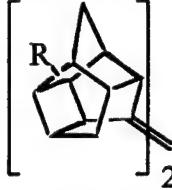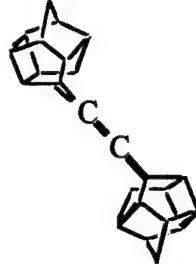
3.2 Improved Routes for the Large-Scale Synthesis of TNAZ

3.2.1 Additions of X-Y Across the N-C(3) σ-bond in 1-aza-3-ethylbicyclo[1.1.0]-butane (38). Model Studies for Developing Novel Routes to 3-Substituted Azetidines. Preliminary studies of the additions of several uniparticulate electrophiles across the strained N-C(3) σ-bond in 1-aza-3-ethylbicyclo[1.1.0]butane (**38**)[4,5] were undertaken. The results of these studies are summarized in Scheme 11.[12,13,36]

Scheme 11

$$X^{\delta+}-Y^{\delta-}$$

38 → **39a-g**

39a: X = NO, Y = ONO$_2$[12]
39b: X = CO$_2$Et, Y = Cl[12]
39c: X = Ms, Y = OMs[12]
39d: X = NO, Y = N$_3$[13]
39e: X = CO$_2$Et, Y = N$_3$[13]
39f: X = NO, Y = NO$_2$[13]
39g: X = SiMe$_3$, Y = N$_3$[36]

12
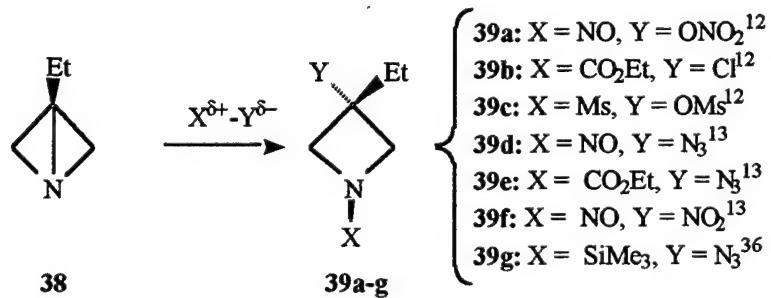
Of particular interest in connection with the development of a new synthesis of TNAZ, we found that reaction of **38** with *in situ* generated aqueous HNO_2 resulted in addition of the elements of HNO_2 across the C(3)-N σ-bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording **39f** (54% yield, Scheme 12). Subsequent oxidation of the *N*-NO functionality by using 98% HNO_3-$(CF_3CO)_2O$ afforded the corresponding *N*-nitramine (**40**, 89% yield).[13] Thus, the reaction sequence shown in Scheme 12 points the way toward a new synthesis of TNAZ, a key feature of which might involve electrophilic addition of the elements of "nitrosonium nitrite", $NO^+ NO_2^-$, across the N-C(3) σ-bond in appropriately functionalized 1-aza-3-ethylbicyclo[1.1.0]butanes.

Scheme 12
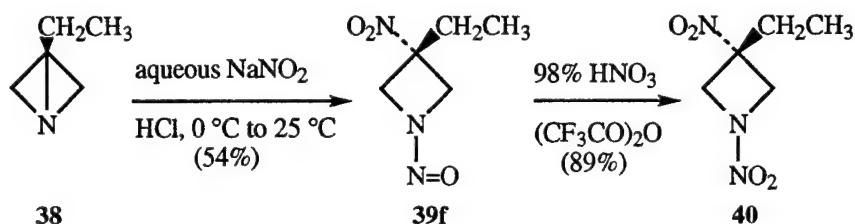
3.2.2 A Novel Synthesis of TNAZ. Success in achieving the synthesis of **40** has been exploited to develop a novel TNAZ synthesis.[37] The key step in this synthesis, shown in Scheme 13, is the formation of 1-azabicyclo[1.1.0]butane, **44**, which is removed rapidly from the reaction medium via azeotropic distillation and is trapped *in situ* in the distillation receiver via its reaction with aqueous $NaNO_2$-HCl, thereby affording *N*-nitroso-3-nitroazetidine (**45**) in low yield.[37]

The method by which **45** is subsequently converted into TNAZ is outlined in Scheme 13. The structure of 1,3-dinitroazetidine (**46**), an intermediate in the conversion of **45** to TNAZ (**47**), was established unequivocally via application of X-ray crystallographic methods. It should be noted that the formation and trapping of **44**, the key intermediate in the reaction sequence shown in Scheme 13, proceeds in poor yield (*ca.* 1%). In addition, the starting material, 2-amino-1,3-propanediol (**41**), although available commercially, is nevertheless very expensive.

In an attempt to address these issues, an alternative reaction sequence was studied which, like the method shown in Scheme 13, preserves the unique approach of formation and trapping of an intermediate 1-azabicyclo[1.1.0]butane. Pertinent results in this regard are outlined in Scheme 14.[37] Thus, 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**50**) was generated by using the

13

method shown in Scheme 14 and is subsequently trapped by *in situ* generated HNO_2. This results in the formation of two *N*-nitrosoazetidines, **51** and **52**, each of which was oxidized[8,38] subsequently to the corresponding *N*-nitro derivative (i.e., **54** and **53**, respectively). The structures of **53** and **54** have been established unequivocally via application of X-ray crystallographic methods. Hydrolysis[39] of **54** produced the corresponding alcohol, **55**, in good yield.* Finally, under the reaction conditions shown in Scheme 14, **55** undergoes retro-Henry reaction,[40] and the resulting α-nitro anion subsequently suffers oxidative nitration *in situ*, thereby affording TNAZ (**47**) in 37% yield from **55**. Full experimental details regarding the syntheses shown in Schemes 13 and 14 have been published.[37]

Scheme 13

_____
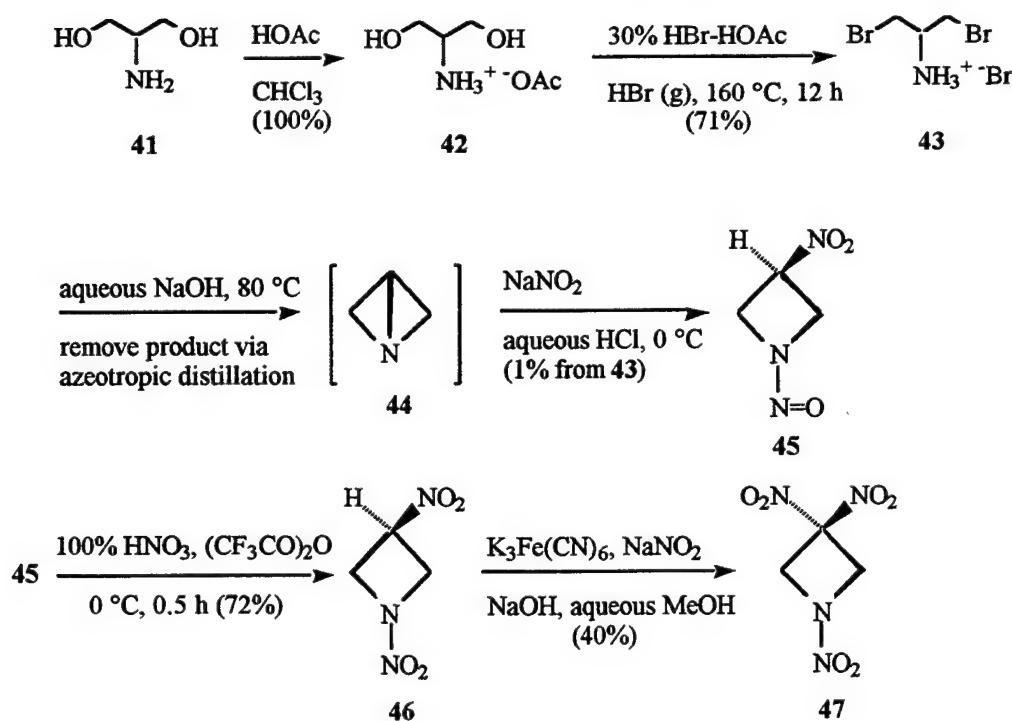
*Dave and co-workers[39] utilized NaI-dimethylsulfoxide-NaHCO$_3$ to oxidize primary alkyl halides to aldehydes. In our hands, application of this regimen to **54** resulted simply in hydrolysis to afford the corresponding primary alcohol (**55**) without concomitant oxidation.

Scheme 14
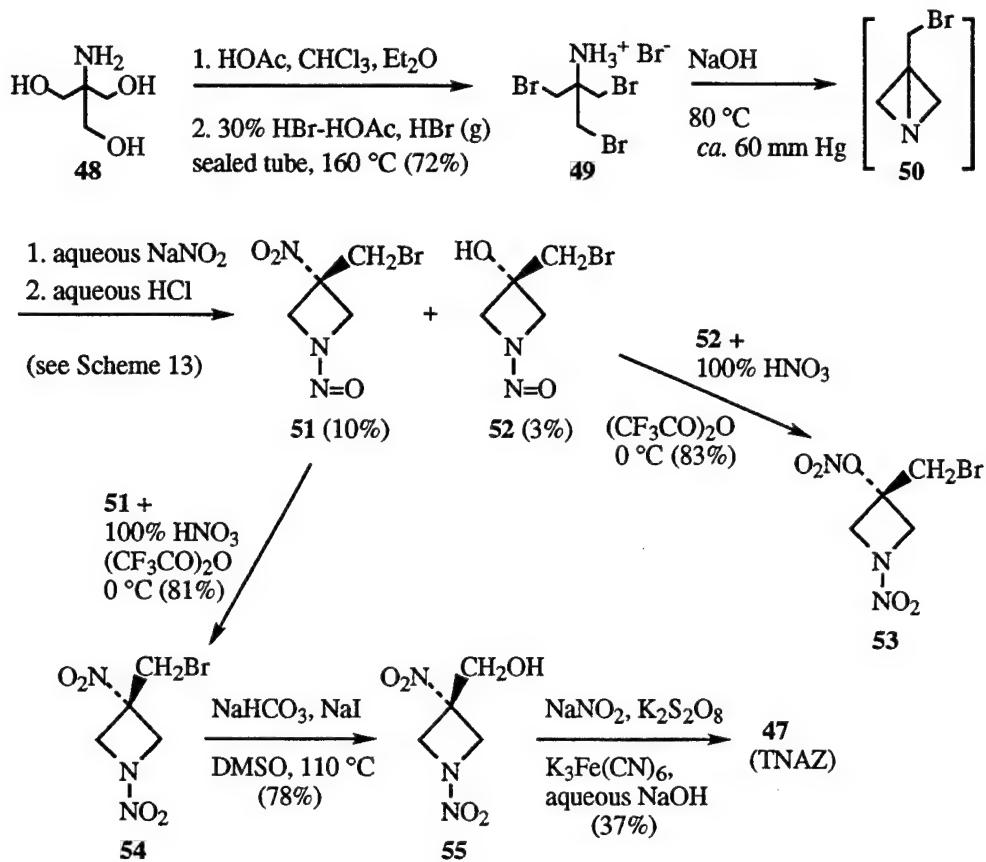
Some important features of the reaction sequence shown in Scheme 14 should be noted. Thus, formation and trapping of the key intermediate in this reaction sequence, i.e., **50**, proceeds in *ca.* 7% overall yield from the starting material, a significant improvement in yield *vis-à-vis* that of the corresponding reaction sequence shown in Scheme 13. In addition, the route shown in Scheme 14 offers the distinct advantage that the 3-bromomethyl functionality in **54** can easily be replaced by NO_2 via a two-step reaction sequence that employs the retro-Henry reaction with concomitant oxidative nitration of a carbanionic intermediate. Finally, in contrast to the prohibitively high cost of **41** (Scheme 13), the starting material for the reaction sequence shown in Scheme 14 [i.e., tris(hydroxymethyl)aminomethane, **48**] is relatively inexpensive. New high-yield routes to appropriately functionalized 1-azabicyclo[1.1.0]butanes continue to be purused, and the chemistry of these new systems as a potentially important class of alkylating agents continues to be studied actively.

3.2.3 Synthesis and Thermal Properties of 1,3-Dinitro-3-(1',3'-dinitroazetidin-3'-yl)azetidine (60). Although TNAZ is a powerful and insensitive explosive, its munitions applications have been limited by the fact that it is a low-melting and relatively volatile solid. For this reason, it would be desirable to form a binary eutectic mixture of TNAZ with another structurally related but less volatile material. To this end, 1,3-dinitro-3-(1',3'-dinitro-azetidin-3'-yl)azetidine (**60**, Scheme 15) has been prepared in the hope that it might form a binary eutectic with TNAZ that would reduce the volatility of the resulting explosive relative to TNAZ without concomitant sacrifice of other advantageous physical and chemical properties of pure TNAZ.

The synthesis of **60** is shown in Scheme 15. The starting material for this reaction sequence, i.e., **56**, was prepared by using the method reported by Hiskey and Coburn.[41] Treatment of **56** with a solution of Br_2 in aqueous base resulted in retro-Henry reaction[40] with concomitant bromination of the resulting nitro-stabilized anion, thereby producing **57**. Subsequent reaction of **57** with $NaBH_4$-EtOH resulted in selective reduction of the carbon-bromine bond in **57**, thereby affording **58** in good yield.

Subsequent base promoted reaction of **58** with KOt-Bu-EtOH resulted in the formation of the corresponding α-nitro carbanion, which was then reacted with **57** to form a mixture of the corresponding 3'-azetidinyl-3-azetidine (**59**) along with unreacted **57** (as determined via analysis of the ^{1}H NMR spectrum of the crude product). This mixture of **57** and **59** could not be separated, either by fractional recrystallization or by column chromatography. Thus, it proved advantageous to react this mixture as obtained with $NaBH_4$. Under these conditions, **57** is reduced to **58**, but **59** remains unaffected. The resulting mixture of **58** and **59** can be separated readily via column chromatography. The structure of **59** was established unequivocally via application of X-ray crystallographic methods. Finally, when refluxed with fuming nitric acid, **59** was converted into the target molecule, **60**, in good yield. The foregoing results, along with a detailed analysis of thermal properties of **60** (alone and in binary mixtures with TNAZ), are summarized in a recent U. S. Air Force Technical Report.[42]

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Scheme 15
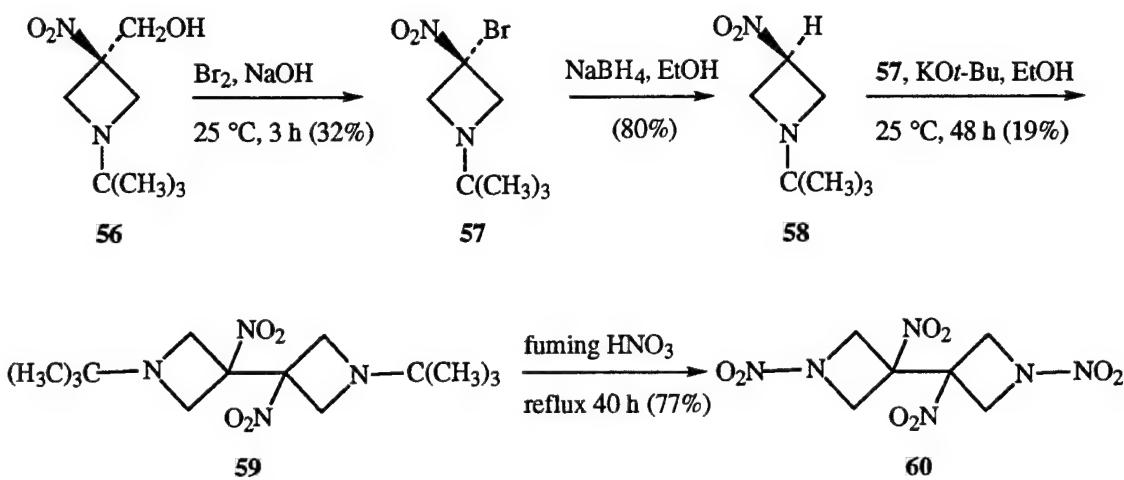
3.3 Structural Studies of Energetic Hydrocarbons and Their Synthetic Precursors

In pursuing the studies described above, it was necessary to characterize several critical intermediates by using single crystal X-ray crystallographic methods. In addition, X-ray structure data was obtained for several cage hydrocarbons and other synthetic intermediates in order to obtain crystal densities and useful structural information (bond lengths, bond angles, etc.). A listing of these structures appears in Figure 1.[43-61]

61[43]   **62**[44]   **63**[44]   **64**[45]

65[45]   **66**[45]   **67**[46]

68[47]   **69**[48]   **70**[48]

71[50]   **72**[51]   **73**[52]

74[53]   **75**[54]   **76**[54]
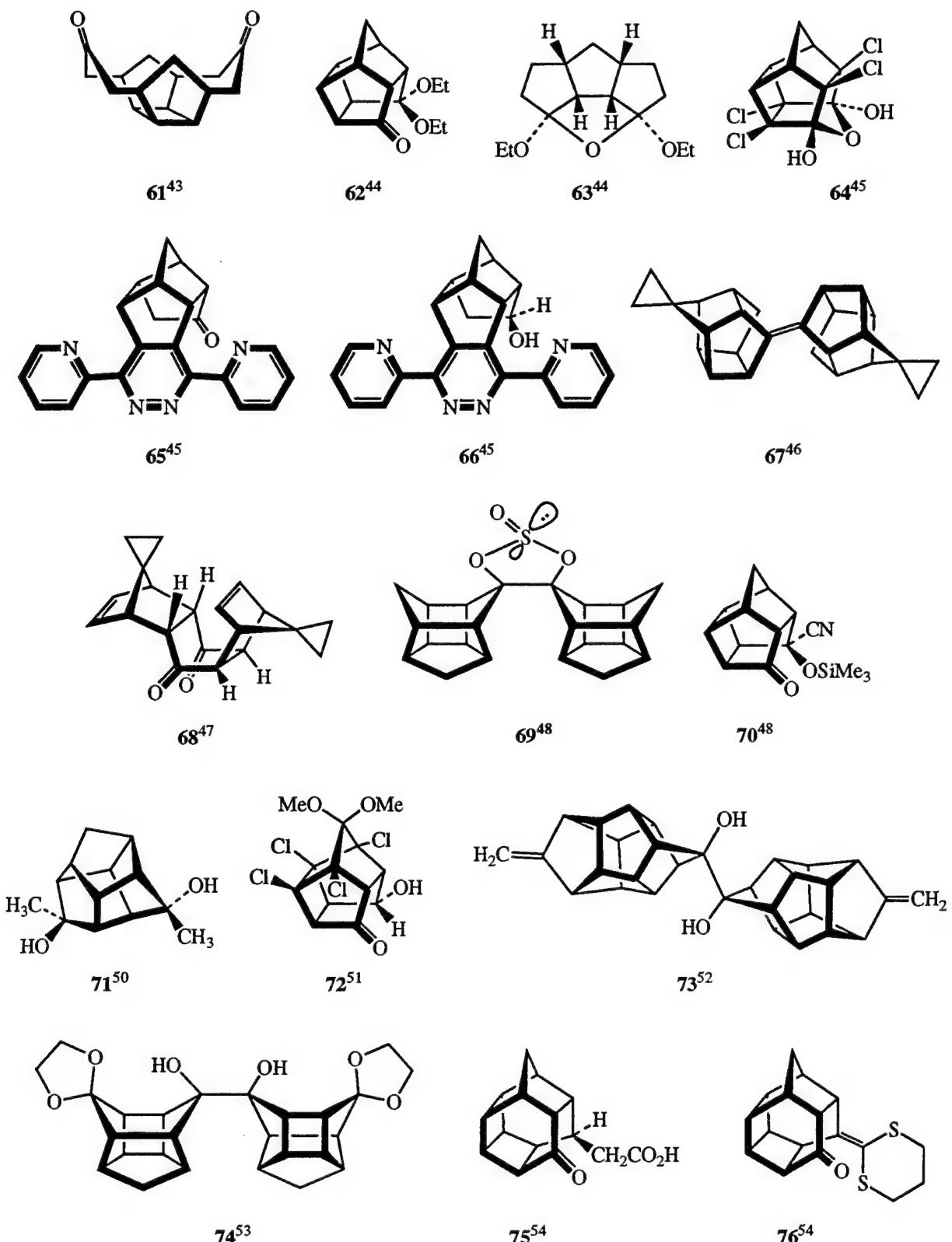
Figure 1
Novel Cage Molecules Which Were Synthesized as Part of This Study
and Whose X-Ray Crystal Structures Have Been Determined and Published

77[54]   **78**[54]   **79**[55]

80[56]   **81**[56]   **82**[56]   **83**[57]

84[57]   **85**[57]   **86**[57]   **87**[57]

**88**[57]   **89**[58]   **90**[59]   **91**[60]

92[61]
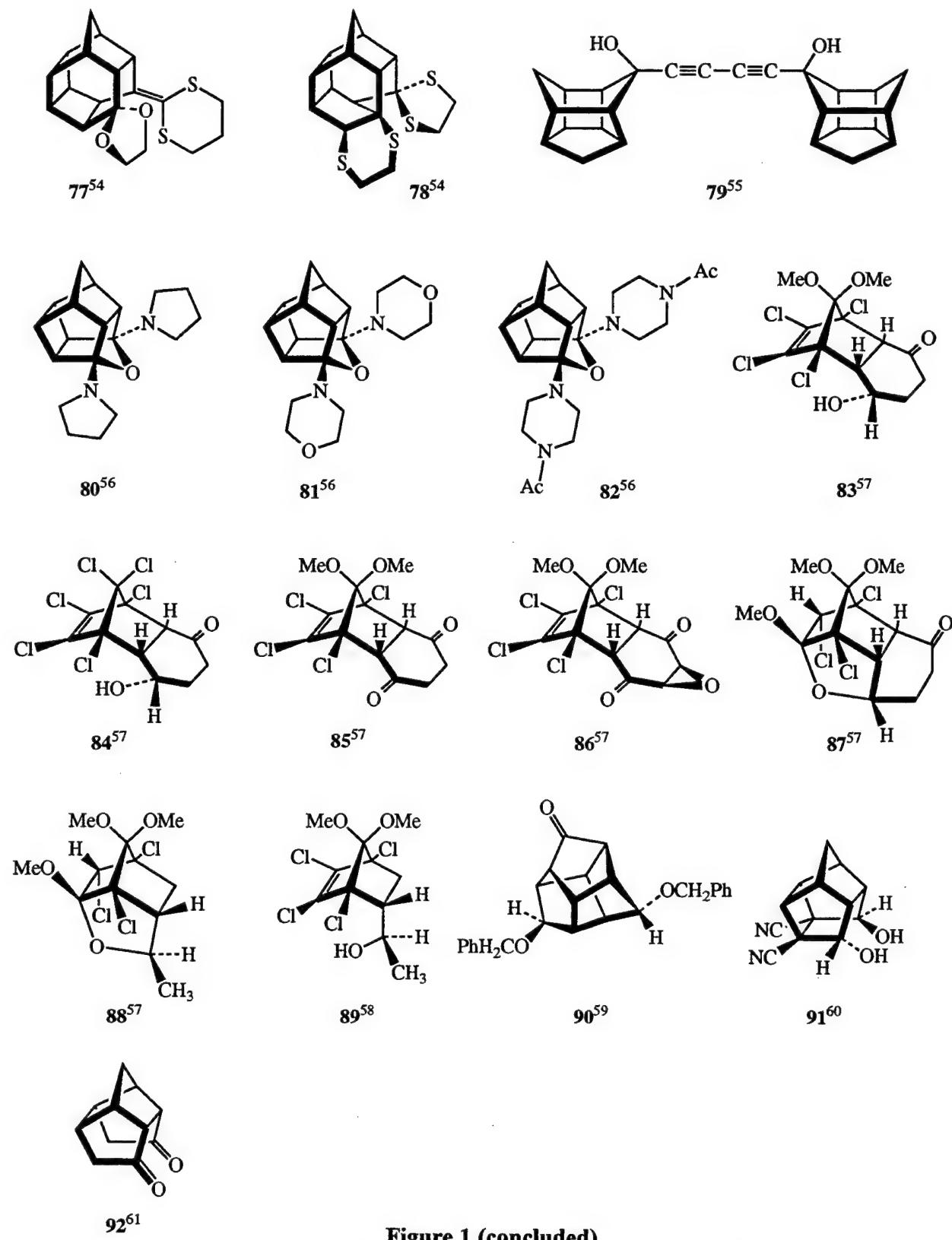
Figure 1 (concluded)
Novel Cage Molecules Which Were Synthesized as Part of This Study
and Whose X-Ray Crystal Structures Have Been Determined and Published

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4.0 CONCLUSIONS

Several new high energy/high density hydrocarbon fuel systems have been synthesized. These include: (i) large-scale syntheses of "PCU alkene dimers" and "methylated PCU alkene dimers" (**2a** and **2b**, Scheme 1); (ii) PCU-derived pinacols **3a**, **4a**, and **4b** and the corresponding "pinacolones" that result via acid promoted rearrangement of these compound (**5**, **6a**, and **6b**, respectively, Scheme 2); (ii) synthesis of an HCTD-derived pinacol (**8**, Scheme 3); (iii) generation and trapping of a PCU-derived vinylidenecarbene (**10a**, Scheme 4); (iv) synthesis of hexacyclo[7.4.0.0^{2,8}.0^{3,7}.0^{4,12}.0^{6,11}]tridecane-10,13-dione ("homosecohexaprismane-10,13-dione", **20**, Scheme 5); (v) synthesis and thermal rearrangement of pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-trideca-2,6-diene (**27**, Scheme 6). In addition, studies of the acid and base promoted rearrangements of hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione (**32**, Scheme 8) have been performed.

In collaboration with Professor Herman Ammon, crystal density modeling calculations have been performed for several polycyclic cage hydrocarbons[31] and polycyclic ethers.[32] Additional collaborations with other laboratories, which were initiated as part of this program, include (i) the use of mixtures of isomeric methylated PCU alkene dimers as crystalline modifiers for TPE-based solid propellant binders (with Dr. Rodney L. Willer, Thiokol Corporation);[21] (ii) evaluation of the fuel and combustion characteristics of mixtures of isomeric PCU alkene dimers as solid fuels in compressible flows (with Professor Corin Segal, University of Florida);[35] (iii) determination of thermodynamic properties of HCTD[33] and PCU[34] (with Professor G. J. Kabo, Belorussian State University, Minsk, Belarus).

Two new syntheses of TNAZ were developed, both of which proceed by way of an intermediate 1-azabicyclo[1.1.0]butane (**44** and **50**, Schemes 13 and 14, respectively).[37]

Finally, X-ray crystal structures have been determined for a variety of cage hydrocarbons (**61-92**, Figure 1).[43-61]

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APPENDIX

Abstracts of publications in peer-reviewed scientific journals that acknowledge Air Force support under Contract No. F29601-82-K-0018

A-1. Marchand, A. P.; Bott, S. G.; Gadgil, V. R.; Watson, W. H.; Krawiec, M.; Kashyap, R. P. Synthesis and Chemistry of a Facially Dissymetric Cage-Condensed p-Benzoquinone: A Synthetic Entry into Novel Doubly-Caged Systems", *Tetrahedron*, **49**, 1993, pp. 6561-6568.

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SYNTHESIS AND CHEMISTRY OF A FACIALLY DISSYMMETRIC CAGE-CONDENSED p-BENZOQUINONE; A SYNTHETIC ENTRY INTO NOVEL DOUBLY-CAGED SYSTEMS

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Absract. The synthesis of a novel caged quinone, **1**, is reported. Diels-Alder cycloaddition of cyclopentadiene to **1** results in the formation of two *endo* adducts, **2a** and **2b**, each of which can be photocyclized to the corresponding "doubly-caged" diketone (**3a** and **3b**, respectively).

A-1

Synthesis and characterization of a novel pentacyclic C_{16} diketone and derivatives

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The syntheses and crystal structures of pentacyclo[9.4.1.0^{5.14}.0^{7.13}.0^{12.15}]hexadecane-3,9-dione (2), a novel C_{16} diketone with potential inclusion ability, and the products of the reaction of 2 with *n*-butyllithium and *meso*-erythritol (i.e., *meso*-1,2,3,4-butanetetrol) are described. Crystal data: $2 \cdot H_2O$, orthorhombic, *Pmmn*, $a = 10.7385(8)$, $b = 9.0188(6)$, $c = 6.8411(4)\,\text{Å}$, $V = 662.55(7)\,\text{Å}^3$, and $R = 0.039$ (379 reflections); 3 (product from reaction with *n*-butyllithium), triclinic, $P\bar{1}$, $a = 8.7192(7)$, $b = 10.9351(8)$, $c = 12.1842(8)\,\text{Å}$, $\alpha = 68.933(5)$, $\beta = 75.850(6)$, $\gamma = 80.309(6)°$, $V = 1047.0(1)\,\text{Å}^3$, and $R = 0.081$ (1811 reflections); 4 (product from reaction with erythritol), triclinic, $P\bar{1}$, $a = 7.7224(8)$, $b = 10.1976(8)$, $c = 10.7021(9)\,\text{Å}$, $\alpha = 85.405(7)$, $\beta = 85.766(8)$, $\gamma = 76.056(7)°$, $V = 814.0(1)\,\text{Å}^3$, and $R = 0.052$ (1471 reflections).

A-2

Structures of two ketals derived from a pentacyclic cage diketone

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The structure of a compound derived from a symmetrical cage diketone in which one of the ketone C=O groups has been converted into a ketal is reported. An investigation into reasons for the selective functionalization resulted in the isolation of a *cis, cisoid, cis* linear triquinane derivative in which both ketones are converted to ketals that share a transannular oxygen atom. Crystal data: **2**, monoclinic, $P2_1/c$, $a = 7.6298(9)$, $b = 7.673(3)$, $c = 22.125(3)$ Å, $\beta = 97.59(1)°$, $V = 1283.9(5)$ Å^3, and $R = 0.048$ (1001 reflections); **4**, triclinic, $P\bar{1}$, $a = 7.3864(9)$, $b = 9.6362(9)$, $c = 10.3889(9)$ Å, $\alpha = 75.749(6)$, $\beta = 76.300(8)$, $\gamma = 83.100(8)°$, $V = 694.8(4)$ Å^3, and $R = 0.088$ (1284 reflections).

Thermodynamic properties of heptacyclotetradecane $C_{14}H_{16}$

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Thermodynamic properties of heptacyclo[$6.6.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane (HCTD) are studied in this work. The molar enthalpy of combustion, found in five experiments is $\Delta_c H_m^\circ(\text{cr}, 298.15\,\text{K}) = -(7743.25 \pm 2.65)\,\text{kJ} \cdot \text{mol}^{-1}$, and the molar enthalpy of formation is $\Delta_f H_m^\circ(\text{cr}, 298.15\,\text{K}) = -(52.59 \pm 3.27)\,\text{kJ} \cdot \text{mol}^{-1}$. The molar enthalpy of sublimation of HCTD was measured with a heat-conduction differential microcalorimeter: $\Delta_{sub} H_m^\circ(333.8\,\text{K}) = (77.99 \pm 0.38)\,\text{kJ} \cdot \text{mol}^{-1}$. The value $\Delta_{sub} H_m^\circ(298.15\,\text{K}) = (79.29 \pm 0.39)\,\text{kJ} \cdot \text{mol}^{-1}$ was obtained using the difference between heat capacities of crystal and gas. Vapour pressure of HCTD was measured by the integral effusion Knudsen method in the range $T = 298\,\text{K}$ to $349\,\text{K}$. As a result we obtained the equation: $\ln(p/\text{Pa}) = -(10078 \pm 146)(\text{K}/T) + (33.64 \pm 0.45)$. The weighted average value of the molar sublimation enthalpy: $\Delta_{sub} H_m^\circ(298.15\,\text{K}) = (79.78 \pm 1.63)$ $\text{kJ} \cdot \text{mol}^{-1}$ was used to calculate the molar enthalpy of formation of gaseous HCTD: $\Delta_f H_m^\circ(\text{g}, 298.15\,\text{K}) = (27.19 \pm 3.65)\,\text{kJ} \cdot \text{mol}^{-1}$. The heat capacity of HCTD was measured by vacuum adiabatic calorimetry ($T = 5\,\text{K}$ to $304\,\text{K}$) and by the triple heat-bridge method ($T = 300\,\text{K}$ to $500\,\text{K}$). One solid-to-solid transition was discovered at $T = 355\,\text{K}$ with molar enthalpy $\Delta_{trs} H_m^\circ = (14.67 \pm 0.73)\,\text{kJ} \cdot \text{mol}^{-1}$. The melting temperature of HCTD is 440 K, and the molar enthalpy of melting is $\Delta_{fus} H_m^\circ = (5.57 \pm 0.28)\,\text{kJ} \cdot \text{mol}^{-1}$. Standard molar thermodynamic functions of HCTD were calculated on the basis of these values at $T = 298.15\,\text{K}$: $S_m^\circ(\text{cr}, 298.15\,\text{K}) = (166.70 \pm 0.70)\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $(\Delta_0^T H_m/T)(\text{cr}, 298.15\,\text{K}) = (84.46 \pm 0.35)\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Phi_m^\circ(\text{cr}, 298.15\,\text{K}) = (82.25 \pm 0.40)\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $\Delta_0^T S_m^\circ(\text{g}, 298.15\,\text{K}) = (337.11 \pm 5.53)\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. I.r. and Raman spectra of HCTD were recorded and vibrational analysis was made. The standard molar thermodynamic properties of HCTD in the gaseous state were calculated in the temperature range from 100 K to 1000 K. The calculated standard molar entropy at $T = 298.15\,\text{K}$: $S_m^\circ(\text{g}) = 336.83\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is in good accordance with the experimental value. The thermodynamic results confirm indirectly the correctness of structural studies of HCTD made by Hargittai *et al.*

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL DENSITY MODELING OF

FOUR $C_{24}H_{28}$ CAGE-FUNCTIONALIZED ALKENES

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Abstract. Titanium-promoted reductive dimerization of methylated pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecan-8-ones, **5a**, **5b**, and **8**, afforded mixtures in each case of "methylated PCU alkene dimers" (**6a-d**, **7a-d**, and **9a**, respectively). Individual isomers have been isolated from these mixtures via column chromatography followed by multiple fractional recrystallization of individual chromatography fractions. Structures of four isomerically pure $C_{24}H_{28}$ alkenes, i.e., **6c**, **6d**, **7c**, and **9a** have been established unequivocally by application of single crystal X-ray crystallographic methods. The crystal density of each alkene (calculated from unit cell parameters) is compared with the results of theoretical density predictions.

A-5

2,8,10,11-tetrachloro-12-oxahexacyclo-[7.2.1.0^{2,8}.0^{3,7}.0^{4,11}.0^{6,10}]dodeca-1,9-diol and disorder and mixed crystals in a system of tetracyclo-[6.3.0.0^{4,11}.0^{5,9}]undecanone and undecanol derivatives

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2,8,10,11-Tetrachloro-12-oxahexacyclo[7.2.1.0^{2,8}.0^{3,7}.0^{4,11}.0^{6,10}]dodeca-1,9-diol is a strained cage molecule containing six five-membered rings and a four-membered ring. Twenty-five of the internal angles are less than 105° with 6 ranging from 89.5(3) to 97.4(3)°. The base promoted reaction of 3,6-dipyridyl-1,2,4,5-tetrazine with tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-3,6-dione yields the monoketone 6,7-[3',6'-di(2"-pyridyl)-4',5'-pyridizino]tetracyclo[6.3.0.0^{4,11}.0^{5,9}]-undecan-2-one. This compound crystallizes in the centrosymmetric space group P2$_1$/n with enantiomers related by a center of symmetry. In the crystal investigated the molecules are disordered with each site containing about 80% of one isomer and 20% of the enantiomer. When the ketone is hydrogenated and the product isolated, two different crystals were found to have a ratio of alcohol to ketone of .71/.29 and .75/.25 or about 3/1. The alcohol and ketone occupy the same sites, but with opposite stereochemistries.

Reactions of 1-Aza-3-ethylbicyclo[1.1.0]butane with Electrophiles. A Facile Entry into New, N-Substituted 3-Ethylideneazetidines and 2-Azetines

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Reaction of 1-aza-3-ethylbicyclo[1.1.0]butane (3) with N_2O_4 under a variety of experimental conditions afforded several products, 4–7, all of which resulted via addition across the strained central C(3)–N σ-bond in 3. The corresponding reactions of $ClCO_2Et$, Tf_2O, and Ms_2O with 3 also have been studied. These reactions provide useful methods for synthesizing N-substituted 3-ethylideneazetidines and 2-azetines.

A-7

Pergamon

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Reactions of Some Sulfur(II)- and Iodine(III)-containing Electrophiles with *endo*-Tricyclo[6.2.1.0²,⁷]undeca-4,9-diene-3,6-dione

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Abstract. Reaction of ArSCl (Ar = phenyl or *ortho*-nitrophenyl) with*endo*-tricyclo[6.2.1.0²,⁷]-undeca-4,9-diene-3,6-dione (**1**) results in *anti* addition across the norbornene carbon-carbon double bond with concomitant aromatization of the cyclohexenedione ring, thereby affording **4** (87%) and **5** (63%), respectively. The corresponding reaction of PhSCl with **1** in the presence of added Ag(I) ·proceeds via polar addition across the norbornene carbon-carbon double bond with concomitant intramolecular nucleophilic trapping of an intermediate episulfonium ion by a distant C=O group, thereby affording **6** (57% yield). The reaction of PhICl$_2$ with **1**, when carried out in the presence of SbCl$_5$ or AgBF$_4$, proceeds with concomitant Wagner-Meerwein rearrangement and aromatization to afford adducts **7a** and **8**, respectively.

Additions of X–Y Across the C(3)–N σ-Bond in 1-Aza-3-ethylbicyclo[1.1.0]butane. Novel Routes to 3-Substituted Azetidines

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Introduction

In 1969, Funke reported the synthesis of 3-ethyl-1-azabicyclo[1.1.0]butane (1) and some aspects of its chemistry.[1] Since that time, relatively little interest has been shown in this unusual ring system. Our own interest in 1 stems from its potential use as a key intermediate in the synthesis of N,3-disubstituted azetidines, which otherwise can be quite difficult to obtain [e.g., via S_N2 displacements on N-substituted-3-(tosyloxy)- (or mesyloxy-) azetidines].[2] Compounds of this type have attracted attention in recent years among members of the energetic materials community.[3] In addition, natural products chemists have been attracted to azetidine alkaloids, a class of strikingly bioactive compounds which have been isolated from marine organisms.[4] Finally, some unusual transformations of 3-functionalized azetidines which are of mechanistic interest have been reported recently.[5]

Previously,[6] we investigated reactions of 1 with a variety of electrophiles, e.g., N_2O_4, $ClCO_2Et$, Tf_2O, and Ms_2O. In each case, the observed reaction product(s) resulted via addition of the reagent, X–Y, across the highly strained C(3)–N σ-bond in the substrate, thereby affording new N,3-disubstituted azetidines. In the present study, we have extended the range of reagents studied in an effort to explore the scope and limitations of reactions of this type. In the course of this work, we performed several of the addition reactions in aqueous solution in an effort to design environmentally benign (i.e., "green") synthetic routes to novel 3-substituted azetidines.

Results and Discussion

Compound 1 was synthesized by using a previously published modification[6] of a literature procedure.[1] Reaction of 1 with *in situ*-generated aqueous HNO_2 resulted in addition of the elements of HNO_2 across the C(3)–N σ-bond with concomitant N-nitrosation of the resulting intermediate azetidine, thereby affording 2 (54% yield,

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Scheme 1
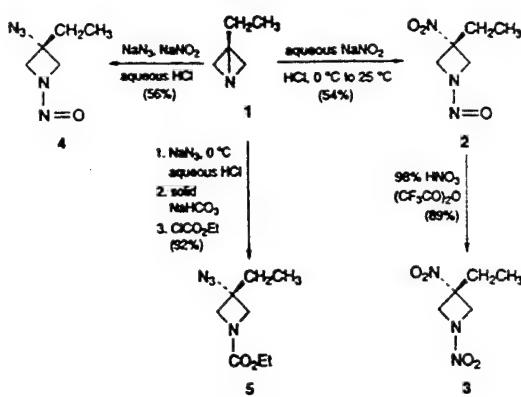
Scheme 2
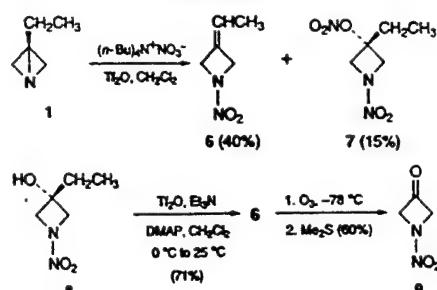
Scheme 1). Subsequent oxidation of the N-NO functionality by using 98% HNO_3–$(CF_3CO)_2O$ afforded the corresponding N-nitramine (3, 89% yield).

Addition of $X^+ N_3^-$ across the C(3)–N σ-bond in 1 was performed in aqueous medium in two separate experiments. Application of the first procedure, which employed aqueous NaN_3 and *in situ*-generated HNO_2, resulted in the formation of 4 (56% yield, Scheme 1). In the second procedure, 1 was reacted with an "azidoformate equivalent" which was generated by sequential reaction of 1 sith *in situ*-generated HN_3 followed by $ClCO_2Et$. Application of this procedure afforded 5 in excellent yield (Scheme 1).

N-Nitro-3-ethylideneazetidine (6) was prepared in two ways. First, 6 was obtained in 40% yield via reaction of 1 with $(n\text{-}Bu)_4N^+ NO_3^-$ and Tf_2O.[7] Compound 7 (15%, Scheme 2) was also formed along with 6 as a product of this reaction. In addition, reaction of azetidinol 8[6] with Tf_2O in the presence of tertiary amines afforded 6 in good yield. Subsequent low-temperature ozonolysis of 6 followed by reductive workup with Me_2S produced N-nitroazetidin-3-one (9), a potential precursor to 1,3,3-trinitroazetidine (TNAZ, an energetic material whose synthesis has attracted considerable attention in recent years[3]).

Compound 11, another potential precursor to TNAZ, was synthesized from oxime 10 which was readily available to us from an earlier study.[6] Thus, sequential reaction of 10 with 100% HNO_3[8] and 90% H_2O_2 produced 11 and 12 (28 and 23% yield, respectively, Scheme 3), which could be separated conveniently by column chro-

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SYNTHESIS OF *exo*-5-AZIDONORBORNENE AND *exo*-2,*exo*-5-DIAZIDONORBORNENE

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Abstract: Polar addition of HN_3 to norbornadiene (1) affords *exo*-5-azido-norbornene (2, 70%). Subsequent azidomercuration-demercuration of 2, performed by using *in situ* generated $Hg(N_3)_2$ followed by reductive demercuration, proceeds stereospecifically to afford *exo*-2,*exo*-5-diazido-norbornane (5, 68% yield).

Structure of a $C_{26}H_{28}$ Alkene Formed via Titanium-Promoted Reductive Dimerization of 4-(Spirocyclopropyl)-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one

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A spiro-fused $C_{26}H_{28}$ "cage" dimer hydrocarbon contains two three-membered rings, two four-membered rings, eight five-membered rings, and two six-membered rings. The molecule is calculated by molecular mechanics to have 902 kJ/mol of strain energy distributed primarily between angle strain (457 kJ/mol) and torsional interactions (368 kJ/mol). Molecular mechanics calculations and a geometry-optimized ab initio calculation are used to analyze the bond lengths and bond angles in the molecule. There is one major discrepancy between observed and calculated distances.

Pergamon

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Diastereofacial Selectivity in Diels-Alder Cycloadditions of Methyl Acrylate to Facially Differentiated Unsymmetrical Cyclohexa-1,3-dienes

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Abstract: The Diels-Alder cycloadditions of methyl acrylate to the unsymmetrical hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadecadienes **1b-f** proceed with a high degree of π-facial stereoselectivity but only moderate regioselectivity. The results of fixed model transition state calculations, performed in an effort to establish the factors which control selectivity in these cycloadditions, are reported.

A-12

The structure of 11,12-bis[spiro(cyclopropyl)]-1,4,4a,5,8,8a,9a,10a-octahydro-1,4:5,8-dimethano-9,10-anthraquinone

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In the solid state the 2:1 Diels–Alder adduct between spiro[4.2]hepta-1,3-diene and p-benzoquinone has a planar cyclohexadione ring with a center of symmetry. Both planar and boat conformations have been observed in similar systems, and the relative stability of the two conformers is of interest. The adduct in the gas phase should contain a mirror plane perpendicular to the cyclohexadione ring; however, a data set collected on a crystal in a capillary resulted in a structure where some bond lengths related by this mirror plane differed by more than 4σ in the solid state. Molecular mechanics, MOPAC, and the Cambridge Structural Data Base were used to investigate the factors influencing the conformation of the cyclohexadione ring and the asymmetry across the noncrystallographic mirror plane. The energy differences between the planar and nonplanar ring system is small, and the conformation is determined by crystal packing. No reason for the bond length asymmetry could be found, and a recollection of data on a crystal exposed to the environment led to a structure with statistically equivalent bond lengths.

A-13

Crystal structure of a bulky cyclic sulfite

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The structure of the cyclic sulfite derived from the reaction of thionyl chloride with *endo*-8-hydroxy-*exo*-8-(*endo*-8'-hydroxypentacyclo[5.4.0.0.^{2,6}.0^{3,10}.0^{5,9}]undec-*exo*-8'-yl)pentacyclo-[5.4.0.0.^{2,6}.0^{3,10}.0^{5,9}]undecane is reported. All bond lengths and angles are consistent with the strained cage geometry. A static disorder of the terminal oxygen was found to be present.

KEY WORDS: Crystal structure, cyclic sulfite, pentacycloundecane-8,11-dione.

Synthesis and structure of *exo*-11-cyano-*endo*-11-(trimethylsilyloxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one

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The crystal structure of an asymmetric pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8,11-dione derivative is reported, in which Me$_3$SiCN has been added across one of the keto groups. The cage structure demonstrates the expected effects of this addition.

A Novel Approach to the Synthesis of 1,3,3-Trinitroazetidine

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Scheme 1

Scheme 2

Introduction

1,3,3-Trinitroazetidine (TNAZ, 1) has received attention in recent years as a new energetic material that is of considerable interest to U. S. military agencies.[1-4] Previously reported routes for synthesizing 1 generally proceed via intermediate *N*,3-disubstituted azetidines, which in each case requires subsequent conversion of the various substituents to $C(NO_2)_2$ groups. We now report a novel approach to the synthesis of 1 which involves electrophilic addition of $NO^- NO_2^-$ across the highly strained C(3)−N σ-bond in 1-azabicyclo[1.1.0]butane and in 3-(bromomethyl)-1-azabicyclo[1.1.0]butane.

In 1969, Funke reported the synthesis of substituted 1-azabicyclo[1.1.0]butanes and some aspects of their chemistry.[5] Since that time, relatively little interest has been shown in this unusual ring system. Recently,[6] we investigated reactions of 2 with a variety of electrophiles, e.g., N_2O_4, $ClCO_2Et$, Tf_2O, and Ms_2O. In each case, the observed reaction product(s) resulted via addition of the reagent, X−Y, across the highly strained C(3)−N σ-bond in the substrate, thereby affording new *N*,3-disubstituted azetidines. In the present study, we have used this approach to synthesize *N*-NO- and *C*-NO₂-containing intermediates which serve as useful synthetic precursors to 1.

Results and Discussion

Compound 2, synthesized by using a previously published modification[6] of a literature procedure,[5] was employed as substrate in a model study.[6b] In our hands, reaction of 2 with *in situ* generated aqueous HNO_2 resulted in addition of the elements of HNO_2 across the C(3)−N σ-bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording 3 (54% yield, Scheme 1). Subsequent oxidation of the *N*-NO functionality by using 98% HNO_3−$(CF_3CO)_2O$ afforded the corresponding *N*-nitramine (4, 89% yield).[6b]

Our success in achieving the synthesis of 4 via the route shown in Scheme 1 pointed the way toward a novel TNAZ synthesis. The key step in this synthesis, shown
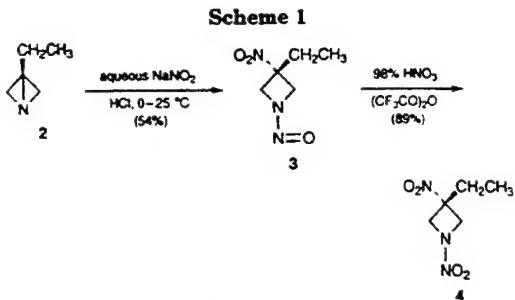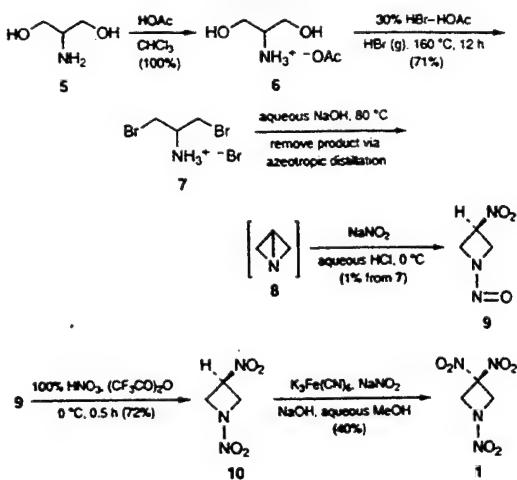
in Scheme 2, is the formation of 1-azabicyclo[1.1.0]-butane, 8, which is removed rapidly from the reaction medium via azeotropic distillation and is trapped *in situ* in the distillation receiver via its reaction with aqueous $NaNO_2$−HCl, thereby affording *N*-nitroso-3-nitroazetidine (9) in low yield. The method by which 9 is converted subsequently into 1 is outlined in Scheme 2. The structure of 1,3-dinitroazetidine (10), an intermediate in the conversion of 9 to 1, was established unequivocally via application of X-ray crystallographic methods. It should be noted that the formation and trapping of 8, the key intermediate in the reaction sequence shown in Scheme 2, proceeds in poor yield (*ca.* 1%). In addition, the starting material, 2-amino-1,3-propanediol (5), although available commercially, nevertheless is very expensive.

In attempting to address these issues, we studied an alternative reaction sequence which like the method shown in Scheme 2 preserves the unique approach of formation and trapping of an intermediate 1-azabicyclo-[1.1.0]butane. Pertinent results in this regard are outlined in Scheme 3. Thus, 1-aza-3-(bromomethyl)bicyclo-[1.1.0]butane (13) is generated by the method shown in Scheme 3 and subsequently is trapped by *in situ* generated HNO_2. This results in the formation of two *N*-nitrosoazetidines, 14 and 15, each of which was oxidized[6,7] subsequently to the corresponding *N*-nitro derivative (i.e., 16 and 17, respectively). The structures of 16 and 17 have been established unequivocally via application of

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Structure of the 1:1 Cycloadduct Formed via Thermal Reaction of Cyclopentadiene with Hexacyclo-[10.2.1.0²,¹¹.0⁴,⁹.0⁴,¹⁴.0⁹,¹³]pentadeca-5,7-diene-3,10-dione †

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Abstract. The structure of the 1:1 cycloadduct which is formed via thermal reaction of cyclopentadiene (CPD) with hexacyclo[10.2.1.0²,¹¹.0⁴,⁹.0⁴,¹⁴.0⁹,¹³]pentadeca-5,7-diene-3,10-dione (1) has been shown unequivocally to possess structure **3b** via application of X-ray crystallographic methods. The results of semiempirical MO calculations (AM1 Hamiltonian), taken together with MMX calculational results and conclusions that arise via FMO-based arguments, suggest that electronic and steric effects each may play an important role in directing the course of the cycloaddition reactions studied herein.

A-17

Pergamon

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Acid Promoted Rearrangement of PCU-derived Pinacols

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Abstract. Three isomerically pure pinacols, i.e., **2**, **3a**, and **3b**, have been prepared via Na promoted reductive coupling of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one (**1a**) and 4-spiro(cyclopropyl)-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one (**1b**), respectively. Acid promoted pinacol rearrangement of each of these PCU-derived pinacols proceeds with exclusive migration of the C(7)-C(8) σ-bond in each case, thereby affording the corresponding pinacolone (**4a**, **5** and **6**, respectively) as the only observed rearrangement product.

A-18

Disorder *versus* symmetry in the helical tubuland inclusion host lattice—a successful trishomocubyl diol probe

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New examples of the helical tubuland diol host family may be targeted for synthesis by consideration of structural rules which result in formation of the specific hydrogen bonding arrangement required. To test crystal engineering requirements of symmetry and substitution in these diols, the 4,7,11-trimethylpentacyclo[6.3.0.0$^{2.6}$.0^{3,10}.0^{5,9}]undecane-4,7-diol isomer **8a** has been prepared and its X-ray structure determined: [C$_{14}$H$_{20}$O$_2$, $P3_1$21, a 12.609(2), c 7.209(2) Å, Z 3, R 0.032]. This diol is a further example of the helical tubuland family despite it lacking C_2 symmetry. Instead, overall C_2 symmetry results in the solid state by means of crystallographic disorder. The C11 methyl group which is equally disposed over its two possible positions reduces the canal unobstructed cross-sectional area to only 8.9 Å^2, but demonstrates that disruption of the lattice type can be avoided provided substituents are placed within the parallel canals. These observations now allow prediction of a much wider range of helical tubuland structures. The diol isomer **8b** [C$_{14}$H$_{20}$O$_2$, $P2_1/c$, a 12.795(1), b 6.4608(4), c 15.003(1) Å, β 111.846(4)°, Z 4, R 0.043] forms a layer structure involving (–OH)$_4$ cycles in common with other diols of closely related structure.

Unusual occurrence of photooxidation of a cage diol

Simon G. Bott,[1,*] Alan P. Marchand,[1,*] and Zenghui Liu[1]

An unusual photooxidation was noted upon photolytic cage closure of a substituted tricyclo[6.2.1.0^{2,7}]undecane-*exo,exo*-diol. The resultant compound, which may be regarded as a mono-reduced pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione, was characterized *via* X-ray crystallography. This species could be reduced to the tricyclo[6.2.1.0^{2,7}]undecane-*endo,exo*-diol under conditions previously shown to be inert for the parent dione.

Structure of the pinacol formed via sodium-promoted reductive dimerization of 12-methyleneheptacyclo-[6.6.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecan-7-one

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The pinacol resulting from sodium promoted reductive coupling of a methyleneheptacyclo-[6.6.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecanone possesses a conformation in which equivalent groups on the pinacol carbon are virtually perpendicular to each other. This rotation minimizes steric interactions, thus the geometries of all the fragments in the molecule are within expected values.

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A Facially Dissymmetric 1,3-Cyclohexadiene as a Dienophile in Diels-Alder Reactions with Polyhalocyclopentadienes†

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Key words: Diels-Alder cycloaddition; π-facial diastereoselectivity; MO calculations

Abstract. Diels-Alder cycloaddition of 1,2,3,4,5,5-hexachloro- and of 5,5-dimethoxy-1,2,3,4-tetra-chlorocyclopentadiene (**2a** and **2b**, respectively) to hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (**1**) occurs in each case with highly stereoselective attack of the diene upon that face of the dienophile which is *anti* to the carbonyl groups. The corresponding *endo,anti* adduct (i. e., **6** and **8**, respectively) is obtained as the exclusive cycloadduct in each case. The structures of **6** and **8** were established unequivocally via X-ray crystallographic methods. The results of AM1 semi-empirical MO calculations for cycloaddition of **1** to **2a** are in accord with experiment.

Structure of a PCU-derived pinacol formed via sodium-promoted reductive dimerization of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione monoethylene ketal

Simon G. Bott,[1]* Alan P. Marchand,[1] and D. Rajagopal[1]

The pinacol resulting from sodium promoted reductive coupling of pentacyclo[5.4.0.0^{2,6}.-0^{3,10}.0^{5,9}]undecane-8,11-dione monoethylene ketal possesses a conformation, dictated by intramolecular hydrogen bonding, that lies midway between eclipsed and staggered. The C–C and C–O distances in the pinacol unit are, respectively, longer and shorter than usual, and all parameters are as expected.

KEY WORDS: Crystal structure; pinacol; reductive dimerization.

Structure of the product formed via Cu(I)-promoted oxidative dimerization of *exo*-8-ethynylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-*endo*-8-ol

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The structure consists of two acetyl-substituted PCU cages linked by a diyne fragment. The conformation about the linker is midway between staggered and eclipsed, and the acetyl groups are somewhat distorted due to the proximity to the bulky cage units.

Rearrangements of Substituted 3-Azidoazetidines:
Unexpected Formation of a Substituted Oxazole

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Thermolysis of neat *N*-carboethoxy-3-azido-3-ethylazetidine (**3**) at 200° under argon produced the corresponding cyclic imine **4** (68% yield). Prolonged refluxing of a mixture of *N*-triflylazetidin-3-one (**7**), sodium azide, and titanium tetrachloride in acetonitrile solvent afforded recovered **7** (25% yield) along with a colorless microcrystalline solid, **8**, mp 104-105° (20% yield), whose structure was established unequivocally *via* application of X-ray crystallographic methods.

Nucleophilic additions of primary and secondary amines to pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione

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The crystal structures of three compounds formed *via* nucleophilic attack of a heterocyclic secondary amine on PCU-8,11-dione, with the concomitant intramolecular attack of one keto oxygen on the carbon of the other ketone, are presented. In all three compounds, the bridging oxygen contains substantial p-character, and the bonds to the "attacking" nitrogen are significantly shorter than would be expected.

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Synthesis and base promoted intramolecular nucleophilic reaction of 8-hydroxy-1,2,3,4-tetrachloro-9,9-dimethoxy-1α,4α,4aα,6,7,8β,8aα-hexahydro-1,4-methanonaphthalene-5(1*H*)-one

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Highly stereoselective sodium borohydride promoted reduction of *endo*-5-acetyl-1,2,3,4-tetrachloro-7,7-dimethoxynorborn-2-ene

Simon G. Bott,[1]* Alan P. Marchand,[1]* Jennifer Bolin,[1] Dongxia Xing,[1] and L. Kathleen Talafuse[1]

Racemic *endo*-5-acetyl-1,2,3,4-tetrachloro-7,7-dimethoxynorborn-2-ene was stereoselectively reduced by sodium borohydride to give only the *S,S* or *R,R* diastereomers. The crystal structure of the product displays no unusual features.

Highly Regioselective Hypervalent Iodine Mediated Ring Cleavage and Ring Expansion Reactions of Some Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane Derivatives

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Abstract: Iodosylbenzene-iodine mediated oxidative fragmentation of 3-hydroxy-4-oxa-5-methyl-hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (1) proceeds with regioselective C(3)-C(10) σ-bond cleavage to afford *exo*-10-iodo-4-oxa-5-methylpentacyclo[5.4.1.0^{2,6}.0^{5,9}.0^{8,11}]dodecan-3-one (4) in 94% yield. The corresponding reaction of 1-hydroxy-12-oxa-pentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]dodecane (6) proceeds with regioselective C(1)-C(11) σ-bond cleavage, thereby affording *endo*-9-(iodomethyl)-5-oxatetracyclo[6.3.0.0^{2,6}.0^{3,10}]undecan-4-one (9, 94% yield). Treatment of *exo*-8-(bromoethynyl)-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]undecane (12) with PhI(OH)(OTs)-I$_2$ resulted in highly regioselective ring expansion to afford 8-[(Z-)bromoiodomethylene]pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,10}]dodecan-9-one (13) as the exclusive reaction product (67% yield). The structures of 4, 9, *exo*-8-ethynyl-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]-undecane (11), and 13 were established unequivocally via single crystal X-ray structural analysis.

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Synthesis and Thermal Rearrangement of Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]trideca-2,6-diene.

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Key words: pentacyclotridecadiene; thermal rearrangement; kinetic study

Abstract. Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]trideca-2,6-diene (**16**) has been synthesized in five steps from 1-hydroxyhexacyclo[6.5.0.0^{2,6}.0^{3,11}.0^{5,10}.0^{9,12}]tridecan-7-one (**10**). Compound **16** undergoes thermal rearrangement to pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene (i. e., "[2.2.1]triblatta-diene", **19**). The intermediacy of *cis,cisoid,cis*-tricyclo[7.4.0.0^{2,7}]trideca-3,5,10,12-tetraene (**18**) in the thermal rearrangement of **16** was inferred via analysis of the ^{1}H NMR spectrum of partially rearranged **16** and subsequently was further established via the results of a trapping experiment (i. e., fluorene was produced when thermal rearrangement of **16** was performed in the presence of 10% Pd/C).

Introduction. As part of an extensive research program which is concerned with the synthesis and

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Strained tridecane cage systems

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Hexacyclo[6.5.0.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tridecane (HCTD) contains two four-membered, two five-membered and two six-membered rings fused into a cage structure which contains about 77.0 kcal/mol of strain energy. Attempts to prepare the thioketal from the diketone of HCTD led to a skeletal rearrangement to produce a cage with one four-membered, four five-membered, and two six-membered rings fused into a cage (RHCTD). The corresponding RHCTD hydrocarbon has a strain energy 13.7 kcal/mol less than that of the starting tridecane (HCTD) which provides the driving force for the rearrangement. The X-ray structures of two HCTD derivatives and one RHCTD derivative are reported. The bond lengths in the three reported structures are normal for cages of this type. The structure of tetracyclo[6.3.0.0^{3,7}.0^{4,11}]undecane-5,10-dione mono(ketene 1',3'-propanedithioacetal) is discussed also.

Structure of a C_2-symmetric bis(benzyloxy)trishomocubanone

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The structure of a bis(benzyloxy)trishomocubanone with molecular C_2 symmetry reveals that substitution of benzyloxy groups has little effect on the trishomocubane cage.

Improved Synthesis of Racemic and Optically Active 4-Hydroxycyclohex-2-en-1-one†

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Abstract: A simple and inexpensive synthetic route which affords S-(-)-4-hydroxycyclohex-2-en-1-one (**1a**) with high stereoselectivity and moderate enantioselectivity is reported. A key step in this procedure involves baker's yeast promoted reduction of $1\alpha,4\alpha,4a\alpha,6,7,8a\alpha$-hexahydro-1,4-methano-naphthalene-5,8-dione (**3**), which affords optically active 8-hydroxy-$1\alpha,4\alpha,4a\alpha,8\beta,8a\alpha$-tetrahydro-1,4-methanonaphthalen-5(1H)-one (**4a**, 80% de, 67% ee) in 32% yield. The absolute configuration of the 3,5-dinitrobenzoate ester of **4a** (i. e., **5a**) was established unequivocally via single crystal X-ray structural analysis.

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Synthesis of (Z)- and (E)-1,2-Di(1-adamantyl)ethene and Their Respective Reactions with Dichlorocarbene[1]

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Abstract. The synthesis of (Z)- and (E)-1,2-di(1-adamantyl)ethene (**1a** and **1b**, respectively) is reported. Compound **1a** reacts with dichlorocarbene to afford (Z)-1-[3-(dichloromethyl)-1-adamantyl],2-(1-adamantyl)ethene (**2**, 27%), (Z)-2,3-dichloro-1,3-di(1-adamantyl)propene (**3**, 20%) and 1,1,2-trichloro-2-(1-adamantyl)chloromethyl-3-(1-adamantyl)cyclopropane (**4**, 21%). The corresponding reaction of **1b** produced (E)-1-[3-(dichloromethyl)-1-adamantyl],2-(1-adamantyl)ethene (**5**, 34%) and (E)-1,2-di[3-(dichloromethyl)-1-adamantyl]ethene (**6**, 5%). The structures of **6**, **7**, and **10** were established unequivocally via application of X-ray crystallographic methods.

Pergamon

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Generation and Trapping of a Caged Cyclopentylidenecarbene

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Abstract. The reactive intermediate that is produced both (i) via reaction of 8-(dibromomethylene)-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (6) with *n*-BuLi-THF and (ii) via the corresponding reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (11) with diethyl diazomethylphosphonate (DAMP) has been shown to be vinylidenecarbene **7a** rather than the corresponding cycloalkyne, **7b**.

SYNTHESIS OF HEXACYCLO[7.4.0.0^{2,8}.0^{3,7}.0^{4,12}.0^{6,11}]TRIDECANE-10,13-DIONE ("HOMOSECOHEXAPRISMANE-10,13-DIONE")

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ABSTRACT: Hexacyclo[7.4.0.0^{2,8}.0^{3,7}.0^{4,12}.0^{6,11}]tridecane-10,13-dione ("homosecohexaprismane-10,13-dione", **8**) has been prepared via a six-step sequence that results in homologation of two of the cyclopentane rings in pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,11-dione, **1**. The structure of **8** has been established unequivocally via single crystal X-ray structural analysis.

Ring-Opening Reactions of 3-Substituted
1-Azabicyclo[1.1.0]butane with Dichlorocarbene[†]

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Reaction of 3-ethyl-1-azabicyclo[1.1.0]butane (**1a**) with chloroform-potassium *tert*-butoxide afforded a ring-opened product, 1,1-dichloro-2-aza-4-ethylpenta-1,4-diene (**4a**), which was characterized *via* conversion to the corresponding *N*-substituted 5-chloro-1,2,3,4-tetrazole, **5a**. Reaction of 3-phenyl-1-azabicyclo-[1.1.0]butane (**1b**) with "Seyferth's reagent" (PhHgCCl$_2$Br) afforded 1,1-dichloro-2-aza-4-phenylpenta-1,4-diene (**4b**), which also was characterized *via* conversion to a tetrazole derivative, i.e., **5b**. Finally, the reaction of **1b** with dichlorocarbene generated under phase transfer conditions (chloroform-sodium hydroxide-TEBA) was studied. At short reaction times (0.5 hour), the major reaction product was **4b**. However, at longer reaction times (20-30 hours), two secondary products, **8** and **9**, were formed which resulted *via* subsequent dichlorocyclopropanation of **4b**.

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On the Mechanism of Acid Promoted Ring Opening of a Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecane-Spiroannulated Oxetane[1]

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Keywords: oxetane, cationic ring opening, 1,5-hydride shift, Wagner-Meerwein rearrangement

Abstract: Specifically deuterated cage-spiroannulated oxetanes **1a** and **1b** each undergo ring opening with concomitant skeletal rearrangement when heated with glacial HOAc in the presence of a catalytic amount of concentrated H_2SO_4. The fate of the deuterium atom in each substrate, as determined via analysis of the NMR spectra of the rearrangement products, establishes unequivocally that a key step in this process proceeds via highly stereoselective intramolecular 1,5-hydride transfer. Copyright © 1996 Elsevier Science Ltd

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Thermodynamic vs. kinetic control in the Diels–Alder cycloaddition of cyclopentadiene to 2,3-dicyano-*p*-benzoquinone

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Diels–Alder cycloaddition of cyclopentadiene (**1a**) to 2,3-dicyano-*p*-benzoquinone (**2a**), when performed in methanol solvent at ambient temperature, proceeds with kinetic control to afford 1α,4α,4aβ,8aβ-tetrahydro-5,8-dioxo-1,4-methanonaphthalene-4a,8a-dicarbonitrile (**7**, 77% yield). However, when this cycloaddition is performed by refluxing an equimolar solution of **1a** and **2a** in benzene for 3 h, the product of thermodynamic control, i.e., 1α,4α,4aα,8aα-tetrahydro-5,8-dioxo-1,4-methanonaphthalene-6,7-dicarbonitrile (**3a**) is obtained in 64% yield. The structure of **3a** was confirmed by an analysis of the reduced intramolecular photocyclization product, **9**.

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Syntheses of Bis- and Tetra-Crowned Clefts and Studies of Their Selectivities in Metal Ion Complexation

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Abstract: A novel "tetra[benzo(18-crown-6)]-crowned cleft" (**2**) and two new "bis[benzo(15-crown-5)]-crowned clefts" (**3** and **4**) have been synthesized. Their respective selectivities in (i) alkali metal picrate extraction into chloroform and (ii) alkali metal perchlorate transport across bulk chloroform membranes have been determined relative to those of appropriate model compounds in each case. The observed picrate extraction selectivity order for **2**, *i. e.* $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, strongly suggests the existence of "sandwich" complexes which result from cooperativity between two spatially proximate benzo(18-crown-6) units in **2** and a guest alkali metal cation. Interestingly, the corresponding extraction selectivity order for **3** and **4** suggests that only 1:1 metal ion-crown ether complexes are formed. For bulk chloroform membranes, bis- and tetra-crowned clefts exhibit much more efficient transport of certain alkali metal perchlorates than do model mono-crown ether compounds. Copyright © 1996 Elsevier Science Ltd

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Synthesis, Characterization and Crystal Density Modeling of Polycarbocyclic Oxiranes

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Abstract. Polycyclic bis-epoxides **5, 6,** and **7** have been synthesized, and their structures established unequivocally via application of single crystal X-ray crystallographic methods. The crystal densities of **2-7** (calculated from X-ray crystallographic data) are compared with the results of theoretical density predictions. Copyright © 1996 Elsevier Science Ltd

Reaction of vinylmagnesium bromide with hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione: Transannular hemiketal formation

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Reaction between vinylmagnesium bromide and the cage dione leads to attack of only one equivalent of Grignard and intramolecular nucleophilic attack on the second ketone. The product compound crystallizes in the monoclinic space group, P2$_1$/a, with $a = 9.509(1)$, $b = 11.071(2)$, $c = 12.492(4)$ Å, $\beta = 104.32(2)°$, and $Z = 4$.

Addition of Trimethylsilyl Azide and of "Mixed Anhydrides" to the N-C(3) σ-Bond in 3-Substituted-1-azabicyclo[1.1.0]butanes[†]

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This paper is dedicated to the memory of Professor Nicholas Alexandrou

Trimethylsilyl azide adds smoothly to the highly strained N-C(3) σ-bond in 3-ethyl-1-azabicyclo[1.1.0]-butane (1) to afford an adduct, 2, that reacts *in situ* with a variety of electrophilic reagents (*i.e.*, ethyl chloroformate, *p*-toluenesulfonyl chloride, benzoyl chloride, acetyl chloride, and oxalyl chloride) to afford the corresponding *N*-substituted-3-azido-3-ethylazetidines 3-7, respectively in 62-72% yield. Similarly, 1 reacts regiospecifically with "mixed anhydrides" (*i.e.*, *p*-toluenesulfonyl acetate, methanesulfonyl acetate, and benzoyl trifluoromethanesulfonate) to afford the corresponding adducts, 8-10, respectively) in 38-68% yield. Reaction of *p*-toluenesulfonyl azide with 1-aza-3-phenylbicyclo[1.1.0]butane (12) produces two products: *N*-(*p*-toluenesulfonyl-3-azido-3-phenylazetidine (13, 15%) and a dimeric product, *N*-(*N'*-*p*-toluenesulfonyl-3'-phenyl-3'-azetidinyl)-3-azido-3-phenylazetidine (14, 28%). Ethyl chloroformate adds to the *N*-C(3) σ-bond in 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (15) to afford *N*-carboethoxy-3-(bromomethyl)-3-chloroazetidine (16) in 73% yield.

Kinetics of the Reaction of Phenylchlorocarbene with an Azabicyclobutane

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Summary. The reaction of phenylchlorocarbene with 3-ethyl-l-azabicyclo[1.1.0]-butane (3) in pentane at 25 °C occurs with a rate constant of 3.2×10^8 $M^{-1}s^{-1}$, most likely via ylide 4. Copyright © 1996 Elsevier Science Ltd

Tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-2,7-dione

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The compound crystallizes in the triclinic space group, P$\bar{1}$, with $a = 6.7702(4)$, $b = 7.0180(4)$, $c = 9.1960(7)$ Å, $\alpha = 92.457(6)$, $\beta = 96.150(6)$, $\gamma = 93.444(5)°$, and $Z = 2$. The structure contains a rather short intramolecular H$\cdots$H contact of 2.26(4) Å.

Electrophilic Additions to Pentacyclic and Tetracyclic Cage Enones; Synthesis of Some Brominated Tetracyclic and Pentacyclic Cage Ketones[†]

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Abstract. Reaction of tetracyclo[6.3.0.0^{3,7}.0^{4,11}]undec-9-en-5-one (**3**) and of pentacyclo[9.2.0.0^{4,8}.0^{5,13}.0^{7,12}]tridec-9-en-3-one (**4**) with PhSCl proceeds via addition across the carbon-carbon double bond with concomitant transannular trapping by C=O of the resulting carbocationic intermediate, thereby affording **5** (50%) and **6** (59%), respectively. The structure of **5** was established unequivocally via application of X-ray crystallographic methods. In addition, syntheses of several new brominated tetracyclo- and pentacycloundecanes (i.e., **7, 9, 11, 12,** and **13**) are reported.

IGNITION CHARACTERISTICS OF A NEW HIGH-ENERGY DENSITY FUEL IN HIGH SPEED FLOWS

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Abstract

"PCU Alkene Dimers", $C_{22}H_{24}$, formed via titanium-promoted reductive dimerization of pentacyclo [5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecan-8-one, are members of a new class of high energy density hydrocarbon fuels. Their ignition characteristics have been evaluated as a solid fuel under conditions of high shear flow. Samples of the dimer were cured with a styrene-polybutadiene copolymer (10% w/w) binder on the test chamber wall and convectively ignited by a gaseous flame in air at Mach 0.12-0.25, stagnation temperature and pressure of 300 K and 150-250 kPa, respectively. Ignition times and rates of heat release were measured. The results indicate that compared with HTPB fuel at same thermodynamic conditions and geometrical configuration the dimer ignition times are one order of magnitude faster. The heat released by combustion by the dimers is more than twice as large. Phase change, ignition and combustion processes of these fuels are investigated with the aid of electron scanning microscope (ESM), high speed photography and pressure and temperature measurements.

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Two Methylated Hexacyclic Cage Diketones

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Abstract

The structures of two methylated hexacyclic cage diketones, 1-methylhexacyclo[$10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}$]-pentadeca-5,7-diene-3,10-dione, $C_{16}H_{14}O_2$, and 13,14-dimethylhexacyclo[$10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}$]pentadeca-5,7-diene-3,10-dione, $C_{17}H_{16}O_2$, have been determined. All bond lengths and angles are consistent with strained-cage geometry.

Structure of 1-(2'-Tosyloxyethoxy)-8-tosyloxy-9,10-anthraquinone

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Abstract

The title compound crystallizes in the monoclinic space group, $P2_1/c$; $a = 12.938(1)$, $b = 11.041(1)$, $c = 19.285(2)$ Å, $\beta = 104.314(8)°$, $Z = 4$. Refinement based on 1660 unique observed reflections converged to $R = 0.0542$. The anthraquinone moiety is distorted due to intramolecular steric hindrance from the tosylate groups.

Key words

anthraquinone, crystal structure, intramolecular hindrance

Structure of a deaza dimer of 4-methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione

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Abstract

The title compound crystallizes in the monoclinic space group, $P2_1/n$; a = 9.0024(5), b = 5.8135(3), c = 15.2232(8) Å, β = 91.153(4)°; Z = 4; R = 0.0496 based on 853 observed, unique reflections. The structure consists of two fused five-membered triazole rings, oriented relative to each other at 152°.

Key words

Acid and Base Promoted Rearrangements of
Hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione

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Abstract. Hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione (3) was synthesized via ring-expansion of hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (1). Reaction of a toluene solution of 3 with a catalytic amount of HCl resulted in extensive skeletal rearrangement, thereby affording 6,7-benzotetracyclo[7.3.0.0^{4,12}.0^{5,10}]dodecane-2,6-dione (4). Subsequent reaction of 4 with 3,6-diphenyl-1,2,4,5-tetrazine (5) afforded a novel molecular cleft, 6. Compound 3 reacted smoothly with ethanolic KOH at ambient temperature (in 3 h) or at reflux (in 0.5 h) to afford a rearranged product, 7. The structures of 3, 4, 5, and 7 were established unequivocally via application of single crystal X-ray crystallographic methods.

Generation and Trapping of *N*-Substituted-3-azetidinylidenecarbenes

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Abstract. The reactive intermediates produced via base-promoted reactions of *N*-tosyl- and *N*-benzhydrylazetidin-3-one (**8a** and **8b**, respectively) with diethyl diazomethylphosphonate (DAMP) have been shown to be vinylidenecarbenes rather than the corresponding cycloalkynes. Thus, *N*-tosylazetidin-3-ylidenecarbene (**9a**) was trapped *in situ* by cyclohexene to afford a cycloadduct, *N*-*p*-toluenesulfonyl-2-(7'-bicyclo[4.1.0]heptanylidene)azetidine (**10**), whose structure subsequently was established unequivocally via single crystal X-ray structural analysis. These results contrast with that reported previously for the corresponding carbocyclic system (i. e., cyclobutanylidenecarbene-cyclopentyne); in the carbocyclic system, the cycloalkyne (rather than the vinylidenecarbene) is trapped *in situ* . The results of semi-empirical MO calculations (AM1 Hamiltonian) for ring expansion of azetidinylidenecarbenes to azacyclopentynes offer clues to the observed difference between the behavior of the heterocyclic and carbocyclic systems.

SYNTHESIS AND THERMAL PROPERTIES OF 1,3-DINITRO-3-(1',3'-DINITROAZETIDIN-3'-YL)AZETIDINE (TNDAZ) AND ITS ADMIXTURES WITH 1,3,3-TRINITROAZETIDINE (TNAZ)

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ABSTRACT

The synthesis of TNDAZ in four steps by starting with N-t-butyl-3-hydroxymethyl-3-nitroazetidine is described. The structures of TNDAZ and of a precursor, N-t-butyl-3-nitro-3-(N'-t-butyl-3'-nitroazetidin-3'-yl)azetidine, have been established unequivocally via application of single crystal X-ray crystallographic techniques. Thermal properties of TNDAZ, TNAZ and admixtures thereof are presented. A binary phase diagram has been predicted computationally and confirmed experimentally by using differential scanning calorimetry and hot stage microscopy. The thermal data support the existence of more than one polymorph for TNDAZ and for TNAZ.